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# SOME FACTORS INFLUENCING THE QUANTITATIVE DETERMINATION OF NITRIC NITROGEN IN THE SOIL

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*From the Utah Agricultural Experiment Station*

For a long time man has been intensely interested in studying the nitric nitrogen of the soil. He has learned that its presence in a soil is necessary for the production of plants, and hence is essential to his own existence. The nitric nitrogen in water is used as a measure of its purity. Recently it has been used in the manufacture of many synthetic compounds; especially is this true of explosives. Civilized nations have therefore come to prize greatly those substances which are rich, or comparatively rich, in nitric nitrogen. Hence, the literature on the subject is voluminous, and many methods have been developed for the determination of nitric nitrogen. Some of these are accurate and workable if used on the substance for which they were intended, and is used under suitable conditions. Others scarcely reach the dignity of qualitative tests. The more important of the methods have been listed and described by others (56, 18). Hence, it is needless for us to consider them in detail here. The majority of the methods have been developed for the determination of nitric nitrogen in water, fertilizers, and various substances comparatively easy to handle. Many are known to be inaccurate when used on substances rich in chlorine, while others are unreliable if used on material high in organic matter. The conditions requisite for the successful use of some of the methods when used on substances high in soluble salts or various colloidal materials are not fully understood; hence, this work has been undertaken with the hope of perfecting a method suitable for the determination of nitric nitrogen in soils, especially those rich in soluble salts.

A method for the determination of nitric nitrogen in soil must be accurate when applied to substances containing either much or little nitric nitrogen. It must be accurate when used on soils having large quantities of soluble salts and those containing large amounts of organic matter. It should be fairly easy of manipulation so that a great number of determinations can be made in a short time.

This last factor would eliminate all of the gasometric methods, for, while accurate, they require considerable time as well as expensive complicated apparatus. The Busch nitron (11) method is not applicable to soil as there are many substances in the soil which interfere (31, 39) in the method, and moreover, the reagent is very expensive. Organic matter interferes in the

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Devarda (14), Tiemann-Schulze (22), Baussingault indigo (23) and Schlösing (38) methods, while organic matter is claimed to be without effect on the Ulsch (41) method.

Results obtained by the electrolytic reduction method vary with a number of factors, namely, the concentration (25) of the acid, strength of current, kind of cathode (36), the deposition of copper at the cathode, whether smooth, spongy, or amalgamated, while chlorides (53) if present interfere.

The sodium amalgam method yields a mixture of products (15) according to the conditions of the experiment. Among these are nitrogen, nitrous oxide, hydroxylamine, hyponitrite and ammonia. The tin reduction method is not reliable in the presence of organic matter, and the reduction to hydroxylamine is not quantitative (28). Furthermore, neither it (32) nor the phenylamine (16) method is applicable in the presence of ferric salts.

The titration of nitrates with ferrous sulfate (5) is not suitable for the determination of small quantities, while chlorides interfere. The results of the brucine method (29) vary with the acid and are not quantitative. The phenoldisulphonic acid method, while probably one of the most accurate for the determination of nitric nitrogen, is not applicable to colored solutions unless first clarified and the organic matter oxidized (49) and soil salts—especially the chlorides and sulfates—cause a loss of nitrates (30, 45).

The iodometric (19, 54) method is unsuited for the determination of nitrates in soil, as many factors interfere and the distillation must be conducted in a current of carbon dioxide. Even under this condition it is far from being as accurate as many of the other methods.

Alberti and Hempel (1) obtained excellent results with the Ulsch method on both pure nitrates and complex manures. L. von Wissel (54) used the Devarda and the Ulsch methods cn solutions containing 16.5 per cent of nitrates. With the Ulsch method he recovered 16.38 per cent, while with that of Devarda he obtained 16.42 per cent. Schmöger (43) in comparative tests with the Raab-Bottcher, Ulsch, Devarda, and Kjeldahl-Foster methods obtained low results. Klut (27) considered the Schulze-Tiemann method best for the determination of nitric nitrogen in water and sewage, with the Ulsch method as a second choice. Bartow and Rogers (4) compared the aluminum reduction, the phenoldisulphonic acid, and the brucine sulfuric acid methods on water of known nitrate content; none of the results were satisfactory, as indicated by many wide differences in the check determinations of the same method. The aluminum reduction method was then carefully investigated and adopted as best for the water containing chlorides. Burgess (27) investigated the aluminum reduction method, using solutions of known nitrate content, and pronounced the method accurate even in the presence of large quantities of soluble salts and organic matter.

From the above-cited literature it may be seen that none of the methods appear to be wholly without objections, but in so far as their use in the presence of large quantities of soluble salts and organic matter is concerned the

aluminum reduction and the Ulsch methods are best. Therefore, in this work we have investigated these two methods, and on account of its extreme accuracy in the absence of chlorides, sulfates, and soluble organic matter, and because of the fact that the conditions of its use have been so carefully investigated (13), we have used, wherever practicable, the phenoldisulphonic acid method for comparison. The methods as used were therefore the aluminum reduction as modified and described by Burgess (10), the phenoldisulphonic acid method as described by Stewart and Greaves (46), and the Ulsch method as described by Ulsch (51).

In place of the specially constructed pear-shaped glass tube used by Ulsch we have used in the neck of the reduction flask a 2-hole stopper through which passes a bent tube which dips into a vessel containing water. Through the other opening in the stopper is passed a separatory funnel. This prevents the loss of any of the nitrate or ammonium sulfate due to the mechanical action of the rapidly evolved hydrogen. It also makes possible the addition of the sulfuric acid in small quantities, thus insuring complete reduction with smaller quantities of both iron and sulfuric acid than when the acid is all added at once. A series in operation is shown in Plate I.

### PREPARATION OF A CLEAR FILTRATE

The investigator of "alkali soils" has difficulty in obtaining a clear filtrate because in the watery extract of such soils we often find the degree of dispersion of the colloidal disperse phase so great and in such a stable form that the solution may be kept for years (7) without flocculation. Furthermore, the particles of such a disperse phase are so small that it is impossible to separate them by means of filtration. It is, however, imperative, especially when using the phenoldisulphonic acid method, that the soil extract be free from colored colloidal material. Still further, no work has been done, so far as we know, to ascertain the influence of these colloids on the various reduction methods. It is quite possible that if the colloidal material be proteinaceous in nature, subsequent treatment may yield from it ammonia which would thus vitiate the results. It is, therefore, essential that we have reliable methods of preparing a clear aqueous solution of the soil nitrates. The ideal method would be one which yielded a clear solution without filtration. This would necessitate the addition of a flocculant to the soil infusion and such a substance should be rapid in action, remove only a minimum quantity of the nitrate from solution and must not interfere with the sensitiveness of the method.

In our search for such an agent we have been guided by two main lines of evidence; first, those substances which have proved most efficient in flocculating other colloids from their dispersing media probably would be most efficient for soil; second, various flocculants have been used and recommended by others workers on similar soils.

The work of Linder and Picton (33) is especially valuable in this connection, as they tested the precipitating powers of various salts on arsenious sulfide solution. Aluminum sulfate was the most efficient compound used, followed by aluminum chloride. Ferric sulfate was only about one-third and calcium salts were only one-fourth as effective, while it required 3200 times as much sodium chloride as aluminum sulfate to bring about the same effect. Furthermore, McGeorge (34) has found aluminum sulfate the most efficient flocculant for clay. But while Wolkoff (58) found the aluminum compounds among the best, there was a great variation, depending upon the soil. This is a fact which may be expected when we recall Hardy's rule that the precipitating power of an electrolyte for a colloid depends on the valence of the ion which carries the electric charge opposite to that of the dispersoid. The colloids found in the soil may be either the electro-negative colloid, clay, or the positive or negative organic colloid.

Buhlert and Fickendey (9) recommended the addition of 2 per cent of sodium chloride, while King and Whitson (26) used potassium alum. But the quantity of alum recommended by them gave with some soils (44) a cloudy solution which had to be filtered before it could be read in the colorimeter. Furthermore, in the presence of sulfates there is a loss of nitrates when the phenoldisulphonic acid method is used. Chamot (12) and co-workers found aluminum cream the best precipitating agent of several tested for organic matter, and that it occasioned no loss of nitrates. But Lipman and Sharp (30) found potassium alum, aluminum cream, and bone black all decidedly unreliable, as they all induced losses of nitrates in the phenoldisulphonic acid method. They found lime to be much more reliable, the losses of nitrates incurred through its use being small. But it must not be used in this method in connection with chloroform, as the double decomposition which takes place under this condition forms chlorides, thus interfering with the accurate determination of nitrates (47). We have used very extensively in our work (46) on soil nitrates the Chamberland-Pasteur filter, which gives a clear solution and occasions only slight losses of nitrates (8).

From the above review it would appear that the most likely flocculants are sodium, potassium, and iron alum, ferric sulfate, lime, finely precipitated calcium carbonate, and talc. Hence, these, together with the Chamberland-Pasteur filter and the centrifuge, were tested on two soils—one a brickyard clay, the other very high in organic matter.

Two grams of each reagent were used in 500 cc. of water containing 100 grams of the soil. The mixtures were shaken for ten minutes in a mechanical shaker and then stood upright. After standing for ten minutes most of the solutions were quite clear and were pipetted off. They were compared, the one with the other, in a colorimeter with the result that a column 100 cm. deep of the lime-teated solution had a turbidity equivalent to a column of the potassium-alum-treated soil 40 cm. deep; the sodium-alum-treated 27 cm.; the ferric-sulfate-treated 26 cm.; and the ferric-alum-treated solution 24 cm. deep.

Both soil-water mixtures, without a flocculant, were clear after centrifuging fifteen minutes at a speed of 1200 revolutions per minute.   Soil-water mixtures to which calcium carbonate or talc had been added were not clear after standing several hours.

The quantity of nitric nitrogen in the clear solution was determined by the aluminum reduction, the Ulsch reduction, and the phenoldisulphonic acid methods.   The average results obtained for the clay soil are given in table 1, while those for the soil high in organic matter are given in table 2.   Determinations were made of the nitric nitrogen in 20 grams of soil, also determinations of the quantity in 20 grams of soil to which had been added 10 mgm. of nitric nitrogen.   In place of reporting the results for each separate determination we have reported the average, together with the standard deviation, according to the following formula:

$$E = \pm \sqrt{\frac{S}{n\,(n-1)}}$$

in which $S$ = the sum of the squares of the difference between each result and the average of all the determinations; and $n$ = the number of determinations in the average.

It was thought unnecessary to use the phenoldisulphonic acid method in the presence of any of the sulfates, as previous workers have shown these substances to interfere with the accuracy of the method.

The results obtained on the soil alone by the Ulsch method are invariably higher than those obtained by either of the other methods.   They are also more uniform in the method of Ulsch than in the other methods.   Furthermore, as may be seen from an examination of the reported standard deviation, the agreement between duplicate determinations is better than with the other methods.   The greatest deviation in the Ulsch method is only ±0.14.   In the aluminum reduction method it is ±0.39, while in the phenoldisulphonic acid method it is ±1.235, but in this case the error is great when calcium carbonate was used as the flocculant and the solutions were very turbid when analyzed.   But even with allowance for this, the variation between duplicates is much greater than with either of the other methods, for we find that the error is great even where the solution was filtered or centrifuged.   These solutions were clear, but the colored soluble colloids which are often in soil solutions, and which it is impossible to remove without oxidation interfere in the phenoldisulphonic acid method.

The average quantity of nitric nitrogen recovered by the Ulsch method where 10 mgm. of nitric nitrogen were added to the soil with the various flocculants was 99 per cent.   The minimum quantity (93 per cent) was obtained where the centrifuge was used, and the maximum (101 per cent) where the iron alum was used.   The average for the aluminum reduction method was 92 per cent, the minimum (88 per cent) where the talc was used, and the maximum (97 per cent) where the iron alum was the flocculant.   The varia-

## TABLE 1

*Milligrams of nitric nitrogen obtained from a heavy clay to which had been added various flocculants*

| FLOCCULATING AGENT | FILTER | CENTRIFUGE | CALCIUM OXIDE | CALCIUM CARBONATE | TALC | POTASSIUM ALUM | SODIUM ALUM | IRON ALUM | FERRIC SULFATE |
|---|---|---|---|---|---|---|---|---|---|
| *Nitric nitrogen found by the aluminum reduction method* | | | | | | | | | |
| Number of determinations in average | 4 | 2 | 4 | 4 | 2 | 3 | 3 | 3 | 3 |
| Nitric nitrogen from soil | 0.38 | 0.64 | 0.32 | 0.32 | 0.32 | 0.46 | 0.28 | 0.25 | 0.28 |
| Nitric nitrogen from soil + 10 mgm. nitric nitrogen | 10.05 | 9.80 | 9.49 | 10.05 | 9.10 | 9.85 | 8.82 | 9.97 | 9.10 |
| Nitric nitrogen recovered | 9.67 | 9.16 | 9.16 | 9.73 | 8.78 | 9.39 | 8.54 | 9.72 | 8.82 |
| Standard deviation | ±0.087 | ±0.28 | ±0.104 | ±0.06 | ±0.14 | ±0.04 | ±0.024 | ±0.39 | ±0.031 |
| *Nitric nitrogen found by the Ulsch reduction method* | | | | | | | | | |
| Number of determinations in average | 3 | 3 | 2 | 4 | 4 | 4 | 4 | 3 | 3 |
| Nitric nitrogen from soil | 0.70 | 0.78 | 0.88 | 0.77 | 0.83 | 0.70 | 0.46 | 0.35 | 0.35 |
| Nitric nitrogen from soil + 10 mgm. nitric nitrogen | 10.37 | 10.10 | 10.51 | 10.81 | 10.70 | 10.37 | 10.33 | 10.45 | 10.08 |
| Nitric nitrogen recovered | 9.67 | 9.32 | 9.63 | 10.04 | 9.87 | 9.63 | 9.87 | 10.09 | 9.73 |
| Standard deviation | ±0.00 | ±0.14 | ±0.00 | ±0.067 | ±0.084 | ±0.029 | ±0.067 | ±0.042 | ±0.084 |
| *Nitric nitrogen found by the phenoldisulphonic acid method* | | | | | | | | | |
| Number of determinations in average | 4 | 3 | 4 | 4 | 4 | | | | |
| Nitric nitrogen from soil | 0.16 | 0.10 | 0.04 | 0.06 | 0.03 | | | | |
| Nitric nitrogen from soil + 10 mgm. nitric nitrogen | 10.87 | 9.20 | 13.10 | 18.28 | 9.05 | | | | |
| Nitric nitrogen recovered | 10.71 | 9.10 | 13.06 | 18.22 | 9.02 | | | | |
| Standard deviation | ±0.52 | ±0.30 | ±0.371 | ±1.235 | ±0.21 | | | | |

## TABLE 2

*Milligrams of nitric nitrogen recovered from a greenhouse loam soil to which had been added various flocculants*

| FLOCCULATING AGENT | FILTER | CENTRIFUGE | CALCIUM OXIDE | CALCIUM CARBONATE | TALC | POTASSIUM ALUM | SODIUM ALUM | IRON ALUM | FERRIC SULFATE |
|---|---|---|---|---|---|---|---|---|---|
| *Nitric nitrogen found by the aluminum reduction method* | | | | | | | | | |
| Number of determinations in average | 3 | 4 | 4 | 3 | 2 | 2 | 4 | 3 | 2 |
| Nitric nitrogen from soil | 1.92 | 1.68 | 2.17 | 1.86 | 1.95 | 1.6 | 2.21 | 1.86 | 2.07 |
| Nitric nitrogen from soil + 10 mgm. nitric nitrogen | 11.19 | 11.76 | 11.83 | 11.39 | 11.00 | 11.91 | 11.49 | 11.50 | 11.00 |
| Nitric nitrogen recovered | 9.27 | 10.08 | 9.65 | 9.52 | 9.05 | 10.30 | 9.28 | 9.62 | 8.92 |
| Standard deviation | ±0.20 | ±0.14 | ±0.093 | ±0.16 | ±0.07 | ±0.05 | ±0.03 | ±0.14 | ±0.07 |
| *Nitric nitrogen found by the Ulsch reduction method* | | | | | | | | | |
| Number of determinations in average | 4 | 3 | 3 | 4 | 3 | 2 | 3 | 3 | 3 |
| Nitric nitrogen from soil | 2.26 | 2.38 | 2.52 | 2.70 | 2.98 | 2.28 | 2.45 | 2.51 | 2.24 |
| Nitric nitrogen from soil + 10 mgm. nitric nitrogen | 12.26 | 12.44 | 12.19 | 12.57 | 12.98 | 12.12 | 12.42 | 11.98 | 11.8 |
| Nitric nitrogen recovered | 10.00 | 10.06 | 9.67 | 9.87 | 10.00 | 9.82 | 9.97 | 9.37 | 9.56 |
| Standard deviation | ±0.09 | ±0.04 | ±0.09 | ±0.07 | ±0.12 | ±0.07 | ±0.02 | ±0.04 | ±0.05 |
| *Nitric nitrogen found by the phenoldisulphonic acid method* | | | | | | | | | |
| Number of determinations in average | 4 | 4 | 4 | 4 | 4 | | | | |
| Nitric nitrogen from soil | 1.77 | 1.50 | 2.81 | 1.79 | 1.65 | | | | |
| Nitric nitrogen from soil + 10 mgm. nitric nitrogen | 14.00 | 10.47 | 14.65 | 11.27 | 10.60 | | | | |
| Nitric nitrogen recovered | 12.23 | 8.97 | 11.84 | 9.48 | 8.92 | | | | |
| Standard deviation | ±0.01 | ±0.49 | ±0.33 | ±0.19 | ±0.28 | | | | |

tion in results where the phenoldisulphonic acid method was used is very great, amounting in the extreme to over 100 per cent. It is interesting to note that where the calcium carbonate was used as the flocculant, usually greater quantities of nitrates were recovered than when the other clarifying agents were used. This may be due to the absorption of some of the nitrate by the flocculated colloid or to the precipitant carrying down mechanically some of the nitrates with the colloids, or in the turbid solutions the fine material left in suspension may contain nitrogen compounds which on subsequent treatment yield ammonia. This latter explanation does not seem plausible on examination of the results given in table 2, where we have a loam soil rich in organic matter. In this series the increase where talc or calcium carbonate is used as the flocculant is no greater than it was with the clay soil, yet the suspended nitrogen-carrying colloid and soluble organic matter would be several times greater in the loam than in the clay soil.

The results, as a whole, for the loam soil are similar to those obtained with the clay. The Ulsch reduction method invariably gives the highest results with the least standard deviation. Moreover, the average nitric nitrogen recovered with the Ulsch method was over 99 per cent of the 10 mgm. of nitric nitrogen which had been added to the soil, while the aluminum reduction method recovers only 95 per cent, and the phenoldisulphonic acid method yields 103 per cent; hence, with both soils the best average and individual results have been obtained with the Ulsch reduction method. Further, there would appear to be a number of objections which may be brought against the aluminum reduction method, as proposed by Burgess. The method, as outlined by him, permits of an appreciable loss of ammonia as one can invariably detect the odor of ammonia on removing the stopper from the reduction tube, and, this being the case, there would be a small loss, and the results which have been reported in the preceding tables indicate that this is a measurable quantity. It is necessary that reduction take place in a thermostat where the temperature can be carefully controlled, in order to obtain even fair results, and it requires several hours for complete reduction. Moreover, even under these conditions we often find tubes in which little or no reduction has taken place, owing to coatings which may be on the fresh aluminum (35), or which may deposit from the soil solution. Hence, the Ulsch reduction method would appear to be better suited to the determination of nitric nitrogen in soil than the aluminum reduction method.

There is nothing in these results which would indicate that a greater error is introduced by the use of the Chamberland-Pasteur filter than by the use of a flocculant, and it is certain that where the phenoldisulphonic acid method is to be used the solution should be prepared by centrifuging or filtering through the Chamberland-Pasteur filter. With the Ulsch method results so far reported indicate that quick lime or alum may be permissible, as they give clear solutions with a considerable saving of time.

But Patten and Snyder (37) found that where lime had been used as the

flocculant, both the phenoldisulphonic acid and the aluminum reduction methods gave low results.   Moreover, they claim that calcium carbonate is just as efficient in clarifying soil solutions as is lime; but this is not in keeping with our experience, for many of the soil solutions with which we have to deal and to which either calcium carbonate or talc have been added are not clear even after standing several hours.   For these reasons we have used the Ulsch method on solutions which have been clarified by both lime and alum to determine the minimum quantity of these flocculants necessary to produce a clear solution and to determine the influence of varying quantities upon the accuracy of the method.   The average results from such a test are given in table 3.   They are the average of four or more determinations.   The determinations were made at different times and on two different soils, hence are not directly comparable the one with the other, but each is comparable where it received different quantities of the respective flocculant.   Both were rich greenhouse soils.

TABLE 3

*Nitric nitrogen found in 100 grams of soil to which various quantities of lime and alum had been added*

| QUANTITY OF FLOCCULANT USED | MILLIGRAMS OF NITROGEN FOUND IN 100 GRAMS OF SOIL IN THE PRESENCE OF | | | |
|---|---|---|---|---|
| | Lime | Standard deviation | Alum | Standard deviation |
| *grams* | | | | |
| 0.5 | 19.00 | ±0.213 | 9.14 | ±0.014 |
| 1.0 | 18.30 | ±0.329 | 9.17 | ±0.014 |
| 2.0 | 18.20 | ±0.403 | 9.31 | ±0.042 |
| 5.0 | 18.00 | ±0.084 | | |

It may be seen from the results reported in tables 1 and 2 that solutions which have been treated with lime gave low results as compared with others which were clarified by the centrifuge or the Chamberland-Pasteur filter, and from the results in table 3 we find that the quantity of nitric nitrogen recovered from a soil varies with the quantity of lime added.   Furthermore, as may be seen from the results reported under "standard deviation," the agreement existing between determinations made on samples containing the same quantities of nitric nitrogen and lime do not agree.   But, even in the presence of lime, in none of our work with the Ulsch method have we obtained such variation as is reported by Patten and Snyder when the aluminum reduction or phenoldisulphonic acid methods are used.   But it is evident that lime does interfere, even in the Ulsch method.

Where alum was used as the flocculant, clear solutions were obtained with 0.5 gram and it is not likely that more than 2 grams would ever be required to clarify the solutions from any soil.   The results obtained with this flocculant are slightly high and can readily be obviated by using in the check on the chemicals the same quantity of alum as has been applied to the soil.   It is

important to note that the variation between different determinations is very small where alum was used as the flocculant.

The low results obtained in the presence of lime are not due to the removal by the lime of colloidal organic material, which, if left in solution, may in subsequent treatment break down and yield ammonia, for similar low results are obtained when lime is added to a pure solution of sodium nitrate, as may be seen from the results given in table 4.

TABLE 4

*Nitric nitrogen recovered from solutions of sodium nitrate containing various flocculants*

| CONTENTS OF SOLUTION USED | NITRIC NITROGEN FOUND | STANDARD DEVIATION |
|---|---|---|
| | *mgm.* | |
| 40 mgm. nitric nitrogen | 39.88 | ±0.150 |
| 40 mgm. nitric nitrogen + 5 grams lime | 38.84 | ±0.599 |
| 40 mgm. nitric nitrogen + 2 grams alum | 39.93 | ±0.128 |
| 40 mgm. nitric nitrogen + 10 grams $CaCO_3$ | 39.09 | ±0.420 |
| 40 mgm. nitric nitrogen + 10 grams talc | 39.50 | ±0.193 |

There is nothing in these results which could be taken to indicate that alum interferes in the Ulsch method any more than does the calcium carbonate and talc. But there is a small loss where the lime is used. The variation between determinations is no greater where the alum was used than in its absence, while where the lime has been used the variation between determinations is comparatively large. Hence, it would appear that potassium alum gives a clear solution with a minimum loss of nitric nitrogen and does not appreciably interfere with the accuracy of the method.

### TIME OF EXTRACTION

The time necessary for water added to a soil to dissolve the nitric nitrogen within that soil may vary greatly with the condition of the soil when the water is added, as well as the treatment given the soil-water mixture. But if the water be not left in contact with the soil for a sufficient length of time, some particles may not be wet; hence, some of the nitric nitrogen will be left unextracted—if left too long, dentrification may take place. Yet we find a large variation in the time recommended by different workers. King and Whitson (26) extracted the soil in a mortar with continual grinding for two minutes, and this is the time which has been used very extensively by us (46). Buhlert and Fickenday (9) agitated the soil with water for one-fourth of a minute at intervals of five minutes for thirty minutes and then filtered. A similar procedure was used by Gutzeit (20), while others (55) extracted for two hours. Sazanov (40) found that longer contact of the water with the soils than enough to allow the soils to settle leads to a loss of nitrates.

In order to obtain more exact information on this subject we have extracted 100-gram portions of soil containing 2 grams of alum with 500 cc. of water for

varying lengths of time.    A rich greenhouse soil was used.    It was mixed with the water in 1000-cc. bottles and shaken in a mechanical shaker for time indicated, then allowed to stand long enough to settle—which was not over ten minutes—and the nitric nitrogen determined.    The average results from four or more determinations are given in table 5.

TABLE 5

*Nitric nitrogen extracted from soil in given time*

| TIME SHAKEN | MILLIGRAMS OF NITRC NITROGEN FOUND IN 100 GRAMS OF SOIL | STANDARD DEVIATION |
|---|---|---|
| *minutes* | | |
| 5 | 21.70 | ±0.02 |
| 10 | 21.70 | ±0.06 |
| 15 | 21.30 | ±0.03 |
| 30 | 21.90 | ±0.03 |
| 35 | 21.90 | ±0.03 |
| 40 | 21.20 | ±0.04 |

These results indicate that nothing is to be gained by shaking the soil with the water longer than five minutes.    But it must be borne in mind that these tests were carried out on finely powdered soil and not upon lumps, and, furthermore, it was thoroughly agitated during the time it was in the shaker.

### RATIO OF SOIL TO WATER

We find different workers vary the ratio of water to soil.    Fricke (17) and Schmidt (42) with fertilizers used one part of sample to fifty parts of water. Litzendorff (31) used one part of soil to two parts of water.    Buhlert (9) and Gutzeit (20) used one part of soil to either one or one and one-half parts of water.    King and Whitson (26) used one part of soil to five parts of water, and this is the ratio which is used by many workers at the present time.    We have made the determinations of nitric nitrogen in soil, and soil to which dried blood was added, using various ratios of water to soil, while all of the other conditions were held the same on all samples.    The average results for four or more determinations are given in table 6.

TABLE 6

*Nitric nitrogen extracted from soil with various quantities of water*

| RATIO OF SOIL TO WATER | MILLIGRAMS OF NITRIC NITROGEN IN 100 GRAMS SOIL | STANDARD DEVIATION | MILLIGRAMS OF NITRIC NITROGEN IN 100 GRAMS SOIL CONTAINING 2 PER CENT DRIED BLOOD | STANDARD DEVIATION |
|---|---|---|---|---|
| 1– 5 | 8.93 | ±0.034 | 9.80 | ±0.056 |
| 1–10 | 8.82 | ±0.034 | 9.10 | ±0.052 |
| 1–15 | 8.70 | ±0.033 | 9.80 | ±0.008 |
| 1–20 | 8.75 | ±0.028 | 9.45 | ±0.028 |
| 1–25 | 8.95 | ±0.029 | 9.38 | ±0.052 |

The difference found is only what could be attributed to experimental error.  Hence, we may conclude that the ratio of soil to water is immaterial, provided we do not add sufficient nitric nitrogen to give a saturated solution.  But it is important that the water in the sample be taken into consideration.  The facts that the same quantity of nitric nitrogen is extracted with the varying quantities of water and that practically 100 per cent of the nitric nitrogen added to the soil is recovered in the various experiments reported in this work, make it very doubtful if Allen and Bonazzi's (2) contentions are justified, that the determination of the nitric nitrogen in the water extract does not give a determination of the nitric nitrogen in the soil.

### USE OF AN ANTISEPTIC

The majority of workers assume that if the soil is to stand in contact with the water any length of time, an antiseptic should be added.  Yet, we have no definite information on the quantity which should be added in order

TABLE 7

*Nitric nitrogen recovered from soil after varying lengths of time*

| TIME | MILLIGRAMS OF NITROGEN RECOVERED IN | | | | | |
|---|---|---|---|---|---|---|
| | 100 grams soil | Standard deviation | 100 grams soil + 20 mgm. nitric nitrogen | Standard deviation | 100 grams soil + 40 mgm. nitric nitrogen | Standard deviation |
| Nitric nitrogen at first................ | 36.85 | ±0.03 | 53.35 | ±0.35 | 72.85 | ±0.16 |
| Nitric nitrogen after 24 hours.......... | 38.53 | ±0.03 | 57.44 | ±0.28 | 74.23 | ±0.07 |
| Nitric nitrogen after  48 hours......... | 34.00 | ±0.02 | 55.28 | ±0.30 | 70.00 | ±0.04 |
| Nitric nitrogen after 120 hours......... | 26.00 | ±0.10 | 50.40 | ±0.06 | 67.20 | ±0.13 |
| Nitric nitrogen after 144 hours......... | 19.90 | ±0.02 | 46.24 | ±0.60 | 53.95 | ±0.22 |

to be effective, and, in many cases, the quantity added may actually accelerate instead of retard or stop the biological transformations going on in the soil.  Moreover, it is not immaterial as to what antiseptic be used, for chloroform (47) used in the presence of lime with the phenoldisulphonic acid method gives inconsistent results.

In order to determine the error which may enter, due to the standing of the soil solution, we treated 100-gram portions of a rich garden soil with water and varying quantities of nitric nitrogen and determined the quantity of nitric nitrogen present after varying lengths of time.  The average results for a number of determinations are given in table 7.

It is interesting to note that no nitrogen is lost from the solution containing only alum during the first twenty-four hours, and the amount lost during the first forty-eight hours where thymol was used amounts to less than 3 mgm.  It must be remembered that this is a soil heavily laden with horse

manure.   The solutions to which thymol had been added lost no nitrogen during the first forty-eight hours, but by the end of one hundred and forty-four hours practically all of the nitric nitrogen had disappeared.   This may have been due to dentrification, or to the rapid multiplication of other micro-organisms within the solutions which were favored by the thymol and had transformed the nitric nitrogen into protein within their bodies.

Where chloroform was used the loss was very slight, even after one hundred and forty-four hours, but it is interesting to note that where the thymol or chloroform was used the results are higher than in their absence.   This is not due to the prevention of bacterial growth, for the results are higher at first in the presence of the antiseptic than in its absence.   And we have found this to be the case in many other tests which are not reported here.   Further-more, in the absence of thymol and chloroform where the 20 or 40 mgm. of nitric nitrogen were added, practically 100 per cent was recovered in the three determinations made during the first forty-eight hours, but where the antiseptic was added, especially the chloroform, the quant'ty recovered is often consid-erably greater or less than that added.

However, the quantity of nitric nitrogen lost from a mixture of soil and fresh horse manure may be considerable, even where the 2 grams of alum have been used as a flocculant, as is seen by the following results.

|  | LIME | ALUM |
|---|---|---|
| Milligrams of nitric nitrogen found at first.............. | 48.34 | 48.94 |
| Milligrams of nitric nitrogen found after 24 hours....... | 45.53 | 41.58 |
| Milligrams of nitric nitrogen found after 72 hours....... | 44.50 | 22.42 |
| Milligrams of nitric nitrogen found after 96 hours....... | 45.80 | 20.30 |

Here we find no loss of nitric nitrogen during the first twenty-four hours either in the soil solution or in that to which sodium nitrate had been added, and even after forty-eight hours the loss was extremely small.   Repeated tests on ordinary fertile soil kept at 24°C. in solutions showed no loss after twenty-four hours and the loss was always very small after forty-eight hours.

That the added antiseptic, if used in too small a quantity, may actually increase bacterial activity and thus increase the loss of nitric nitrogen, may be seen from the results reported in table 8.   In this series a soil rich in manure was used; to one set was added only the flocculant—2 grams of alum—to the second 2 grams of alum plus 2 cc. of a saturated solution of thymol, and to the third 2 grams of alum plus 0.5 cc. of chloroform.   All were kept at a temperature of 24°C.   The results as reported are the average of a number of determinations.

While in this case we are dealing with solutions with optimum conditions for dentrification, the loss in the presence of lime is small, but in the case of the alum it is appreciable.   This, however, is a soil extremely rich in nitric nitrogen and the results probably represent a maximum dentrification, and

TABLE 8

*Nitric nitrogen in soil after varying lengths of time*

| TREATMENT | AT FIRST | STANDARD DEVIATION | AFTER 24 HOURS | STANDARD DEVIATION | AFTER 48 HOURS | STANDARD DEVIATION | AFTER 144 HOURS | STANDARD DEVIATION | AFTER 168 HOURS | STANDARD DEVIATION |
|---|---|---|---|---|---|---|---|---|---|---|
| Soil + 2 grams alum | 48.00 | ±0.03 | 47.63 | ±0.025 | 45.20 | ±0.04 | 35.00 | ±0.09 | 33.60 | ±0.00 |
| Soil + 2 grams alum + 20 mgm. nitric nitrogen | 67.96 | ±0.05 | 67.26 | ±0.025 | 65.44 | ±0.03 | 58.14 | ±0.09 | 55.34 | ±0.05 |
| Soil + 2 grams alum + 40 mgm. nitric nitrogen | 89.68 | ±0.06 | 87.28 | ±0.033 | 84.34 | ±0.06 | 77.01 | ±0.05 | 72.85 | ±0.57 |
| Soil + 2 grams alum + thymol | 49.04 | ±0.05 | 49.00 | ±0.07 | 48.30 | ±0.10 | 4.00 | ±0.22 | 5.00 | ±0.57 |
| Soil + 2 grams alum + thymol + 20 mgm. nitric nitrogen | 69.36 | ±0.05 | 67.68 | ±0.03 | 67.96 | ±0.10 | 4.40 | ±0.19 | 4.00 | ±0.05 |
| Soil + 2 grams alum + thymol + 40 mgm. nitric nitrogen | 89.26 | ±0.05 | 88.26 | ±0.068 | 8.26 | ±0.04 | 1.40 | ±0.35 | 4.00 | ±0.00 |
| Soil + chloroform | 51.80 | ±0.10 | 51.80 | ±0.03 | 51.30 | ±0.04 | 43.40 | ±0.04 | 37.80 | ±0.00 |
| Soil + chloroform + 20 mgm. nitric nitrogen | 71.94 | ±0.08 | 71.87 | ±0.09 | 71.46 | ±0.05 | 60.66 | ±0.11 | 57.55 | ±0.07 |
| Soil + chloroform + 40 mgm. nitric nitrogen | 88.46 | ±0.11 | 91.06 | ±0.04 | 88.26 | ±0.14 | 80.84 | ±0.30 | 72.86 | ±0.17 |

such activity would never be reached with average soil. But even this loss can be prevented by the use of chloroform, as may be seen from table 9 which shows the quantities of nitric nitrogen recovered from a soil manure mixture in water at 24°C. after varying lengths of time.

By the end of three hours the soil to which no antiseptic had been added had lost one-half of its nitric nitrogen, while during twenty-four hours it had been reduced to 0.83 mgm. The soil to which the 2 grams of alum only had been added slowly lost its nitric nitrogen so that after seventy-two hours its amount had been reduced to one-half that present at the beginning. Where the chloroform was added the quantity remains fairly uniform through-

TABLE 9

*Nitric nitrogen from soil and manure after varying lengths of time*

| TREATMENT | MILLIGRAMS OF NITRIC NITROGEN FOUND | | | |
|---|---|---|---|---|
| | In beginning | After 24 hours | After 48 hours | After 72 hours |
| Soil, no antiseptic | 3.064 | 0.826 | 0.49 | 0.56 |
| Soil + 2 grams alum | 3.117 | 2.732 | 2.59 | 1.96 |
| Soil + 2 grams alum + 0.5 cc. $CHCl_3$ | 3.067 | 2.980 | 3.06 | 3.22 |
| Soil + 2 grams alum + 1.0 cc. $CHCl_3$ | 2.956 | 2.840 | 2.90 | 2.91 |
| Soil + 2 grams alum + 2.0 cc. $CHCl_3$ | 2.800 | 3.010 | 2.90 | 2.89 |
| Soil + 2 grams alum + 3.0 cc. $CHCl_3$ | 2.790 | 2.910 | 2.93 | 3.16 |

out the seventy-two hours and it would appear that 0.5 cc. of chloroform is ample to prevent loss of nitric nitrogen. But it has been our experience that where the analyses are completed immediately, more concordant results are obtained without than with chloroform. The average results on both, rich soil and a soil manure mixture, are shown graphically in figure 1. In this the quantity of nitric nitrogen in the soil at the beginning of the experiment has been considered as 100 per cent.
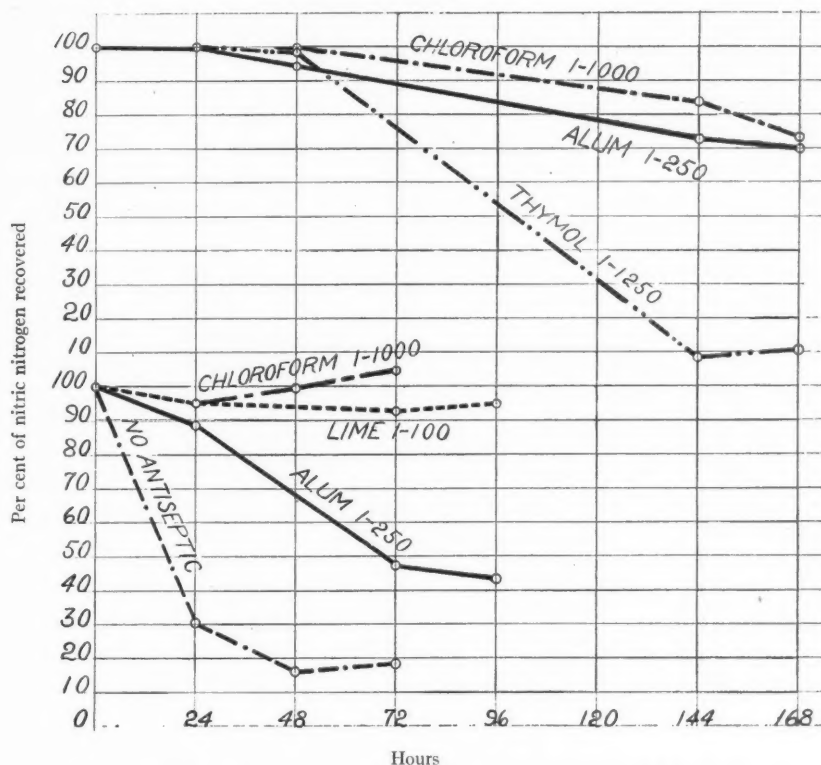


Fig. 1 Curves showing per cent of nitric nitrogen recovered in sample of soil treated by different antiseptics after varying lengths of time.

The soil with 2 grams of alum during the first twenty-four hours lost 0.8 per cent of its nitric nitrogen, while those to which chloroform or thymol had been added lost none. By the end of one hundred and sixty-eight hours the soil plus 2 grams of alum had lost 30 per cent, the soil with the chloroform had lost 27 per cent, while that to which the thymol had been added had lost 89.8 per cent of its nitric nitrogen. The loss from the horse manure soil

mixture—with no antiseptic—during the first twenty-four hours was 73 per cent, but it was very low in the presence of the antiseptics.

From all the results reported it would appear that where the alum is used as a flocculant no other antiseptic is necessary unless the solutions are to remain several hours. The losses of nitrogen reported in most of this work are maxima and probably would never be duplicated in regular work, as the soil contained such large quantities of nitrates and organic matter of fresh horse manure. Moreover, the solutions were kept in an incubator at 24°C. during various intervals. Hence, it would appear that, under ordinary conditions, where the time in which the soil is in the water is short, and the temperature comparatively low, no loss would result with ordinary soil where the 2 grams of alum had been added.

### QUANTITY OF ACID AND IRON

Ulsch (50) in his original method recommends that the nitrate-carrying substance be dissolved in 25 cc. of water, and this reduced with 5 grams of

TABLE 10

*Nitric nitrogen from 20 grams of soil plus 40 mgm. of nitric nitrogen with different quantities of sulfuric acid and iron*

| IRON USED | H$_2$SO$_4$ USED | NITRIC NITROGEN USED | STANDARD DEVIATION | PERCENTAGE RECOVERED |
|---|---|---|---|---|
| *grams* | *cc.* | *mgm.* | | |
| 5 | 10 | 35.76 | ±0.51 | 82.62 |
| 5 | 20 | 40.21 | ±0.30 | 92.90 |
| 5 | 25 | 42.45 | ±0.58 | 98.08 |
| 5 | 30 | 42.90 | ±0.10 | 99.10 |
| 6 | 20 | 42.73 | ±0.31 | 98.72 |
| 6 | 25 | 42.24 | ±0.50 | 97.60 |
| 6 | 30 | 42.59 | ±0.06 | 98.40 |

iron and 10 cc. of dilute sulfuric acid (1 to 2). Later (51) he found 10 grams of iron and 10 cc. of dilute sulfuric acid (sp. gr. 1.35), sufficient to reduce 0.5 gram of potassium nitrate. Schenke (41) recommends 4 grams of iron and 12 cc. of sulfuric acid (sp. gr. 1.35). Work at the New Jersey Station (3) indicates that 2 grams of iron and 5 cc. of sulfuric acid was sufficient for 1-gram samples of any fertilizer, while the Street (48) modification requires 2 or 3 grams of reduced iron and 10 cc. of sulfuric acid (one part of acid to one of water). Our experience has been that the best results are obtained when the ratio between the iron and acid is large, as is brought out by the results in table 10. In this work the quantity of nitric nitrogen determined was that extracted from 20 grams of a rich soil to which had been added 40 mgm. of nitric nitrogen. The results are the average of four or more determinations. Repeated determinations had yielded from 20 grams of the soil 3.28 mgm. of nitric nitrogen; hence, the quantity of nitric nitrogen actually placed in the reduction flask was 43.28 mgm.

Here we find the greatest quantity of the nitric nitrogen was recovered where 5 grams of iron were used with 30 cc. of sulfuric acid (sp. gr. 1.35). The results vary with the method of adding the acid, the reduction being, more complete when the acid is slowly added by means of a dropping funnel as previously outlined. But in no case were we able to obtain concordant results when the quantity of acid used was such as to leave considerable undecomposed iron in the reduction flask.

The quantity of iron necessary will vary with the quantity of nitric nitrogen to be reduced and also with the grade of iron used, as may be seen from the results reported in table 11. Here we have used three different grades of iron and 25 cc. of sulfuric acid with the soil and nitrates as in previous experiments.

The "iron-by-hydrogen 90 per cent" yielded the same quantity of nitric nitrogen when 7 grams were used as when 5 grams were used. But the 80 per cent and the alcoholized iron both yielded more nitric nitrogen with the

TABLE 11

*Nitric nitrogen recovered with various grades and quantities of iron*

| KIND OF IRON | IRON USED | NITRIC NITRO- GEN RECOVERED | STANDARD DEVIATION | PERCENTAGE OF NITRIC NITROGEN RE- COVERED |
|---|---|---|---|---|
| | grams | mgm. | | mgm. |
| Iron by hydrogen, 90 per cent..... | 5 | 42.80 | ±0.11 | 98.90 |
| Iron by hydrogen, 90 per cent..... | 7 | 42.69 | ±0.07 | 98.52 |
| Iron by hydrogen, 80 per cent..... | 5 | 41.92 | ±0.22 | 96.61 |
| Iron by hydrogen, 80 per cent..... | 7 | 42.95 | ±0.14 | 99.00 |
| Alcoholized iron................. | 5 | 40.03 | ±0.17 | 90.20 |
| Alcoholized iron................. | 10 | 42.27 | ±0.25 | 97.05 |

larger quantities of iron. This is probably due to 5 grams of either 80 per cent or alcoholized reagent not containing enough elementary iron for the complete reduction of 40 mgm. of nitric nitrogen. None of the samples of iron tested contained impurities which would yield ammonia, for repeated tests failed to reveal the presence of ammonia, ammonium compounds, or nitric nitrogen; nor did these samples of iron contain a reducible organic compound as reported by Brandt (6) and later by Hartwell and Wheeler (21).

Moreover, it is certain that 5 grams of 90 per cent "iron-by-hydrogen" is ample for the reduction of 40 mgm. of nitric nitrogen, but where lower grades are used more will be necessary. Even when 10 grams of the alcoholized iron were used we failed to recover all of the nitric nitrogen, and it would not be practicable to use larger quantities, as it introduces many difficulties in technique.

#### TIME NECESSARY FOR REDUCTION

The time required for complete reduction varies with the temperature. Ulsch (50) found that the percentages of nitric nitrogen recovered when

0.5-gram portions of potassium nitrate were reduced at varying temperatures with appropriate quantities of iron and sulfuric acid were as follows:

| | Per cent reduced |
|---|---|
| 20°C. for two hours.............................................. | 95 |
| 30°C. for two hours.............................................. | 97 |
| 40°C. for two hours.............................................. | 100 |
| 90°C. for eight minutes.......................................... | 99.5 |
| 100°C. for two minutes.......................................... | 98.9 |

This is in keeping with the results obtained by us where 20 mgm. of nitric nitrogen were reduced at varying temperatures.

The results shown in table 12 would indicate that the reduction is not complete even after four hours at the lower temperature, but that when the solution is boiled all of the nitric nitrogen is recovered. It is important to

TABLE 12

*Percentages of nitric nitrogen recovered in various reductions*

| TEMPERATURE | TIME | PERCENTAGE OF NITRIC NITROGEN RE-COVERED | STANDARD DEVIATION |
|---|---|---|---|
| | *hours* | | |
| 25°C.......................................... | 2 | 93.00 | ±0.58 |
| 50°C.......................................... | 2 | 94.50 | ±0.15 |
| 25°C.......................................... | 3 | 91.40 | ±0.62 |
| 50°C.......................................... | 3 | 96.65 | ±1.00 |
| 25°C.......................................... | 4 | 97.70 | ±0.12 |
| 50°C.......................................... | 4 | 98.75 | ±0.03 |
| Cold ½ hour. Boiled until hydrogen ceased..... | | 99.75 | ±0.04 |
| Cold, then boiled ten minutes................. | | 99.75 | ±0.04 |

note that the variation between the determinations is very great when the temperature is low and the time given for reduction short, but where the reduction was conducted at 50°C. for four hours, or by boiling the solution, the agreement was very good. Therefore, it would seem to be advisable to finish the reduction at boiling temperatures and to return the liquid carried over mechanically to the reduction flask before the evolution of hydrogen has ceased, so as to insure reduction of any nitric nitrogen which may have been carried over by the first rapid evolution of hydrogen.

INFLUENCE OF VARIOUS SALTS

Many of the solutions obtained from the arid and semi-arid soils are very rich in soluble salts; hence, it is necessary that the method used for the determination of nitric nitrogen be reliable even when used on solutions containing large quantities of soluble salts. Therefore, we have made determinations using solutions to which had been added various salts which may occur in the soil solutions. These naturally fall into three series treated as follows:

The first series contained 20 mgm. of nitric nitrogen in 500 cc. of water; the second, 20 mgm. of nitric nitrogen and 5 grams of one of the salts given in table 13 in 500 cc. of water; the third series contained 20 mgm. of nitric nitrogen, 5 grams of one of the salts, and 100 grams of soil and the 500 cc. of water.   The soil used in this last series, as an average of ten determinations, had yielded 0.728 mgm. of nitric nitrogen from 100 grams of soil.

The average quantity of nitric nitrogen recovered from the nitric nitrogen solution was 98.5 per cent, exactly the average quantity recovered where the

TABLE 13

*Milligrams of nitric nitrogen recovered from various solutions*

| SOLUTION CONTAINING 20 MGM. OF NITRIC NITROGEN | STANDARD DEVIATION | SALT ADDED | 20 MGM. NITRIC NITROGEN PLUS 1 PER CENT SALT | STANDARD DEVIATION | 20 MGM. NITRIC NITROGEN PLUS 100 GRAMS SOIL PLUS 1 PER CENT SALT | STANDARD DEVIATION |
|---|---|---|---|---|---|---|
| 20.16 | ±0.00 | NaCl | 19.80 | ±0.03 | 20.36 | ±0.10 |
| 19.62 | ±0.00 | $Na_2SO_4$ | 19.60 | ±0.00 | 20.46 | ±0.17 |
| 19.82 | ±0.03 | $Na_2CO_3$ | 20.10 | ±0.14 | 19.98 | ±0.12 |
| 19.47 | ±0.04 | KCl | 19.47 | ±0.03 | 19.75 | ±0.00 |
| 19.79 | ±0.03 | $K_2SO_4$ | 19.58 | ±0.09 | 20.07 | ±0.03 |
| 19.61 | ±0.13 | $K_2CO_3$ | 19.79 | ±0.03 | 20.50 | ±0.09 |
| 19.71 | ±0.01 | $Ca Cl_2$ | 19.93 | ±0.07 | 20.07 | ±0.03 |
| 19.71 | ±0.05 | $CaSO_4$ | 19.79 | ±0.07 | 20.27 | ±0.17 |
| 19.61 | ±0.14 | $CaCO_3$ | 19.47 | ±0.08 | 20.18 | ±0.08 |
| 19.79 | ±0.09 | $MgCl_2$ | 19.61 | ±0.06 | 20.18 | ±0.06 |
| 19.65 | ±0.07 | $MgSO_4$ | 19.79 | ±0.09 | 20.03 | ±0.09 |
| 19.71 | ±0.05 | $MgCO_3$ | 19.82 | ±0.09 | 20.13 | ±0.05 |
| 19.55 | ±0.04 | $MnCl_2$ | 19.57 | ±0.05 | 20.13 | ±0.00 |
| 19.68 | ±0.04 | $MnSO_4$ | 19.75 | ±0.00 | 20.25 | ±0.03 |
| 19.60 | ±0.06 | $MnCO_3$ | 19.63 | ±0.03 | 20.09 | ±0.03 |
| 20.13 | ±0.04 | $FeCl_3$ | 20.12 | ±0.05 | 20.02 | ±0.05 |
| 19.88 | ±0.12 | $Fe_2(SO_4)_3$ | 19.78 | ±0.17 | 19.22 | ±0.17 |
| 20.10 | ±0.09 | $Na_2CO_3$ + $Na_2 O_4$ | 19.99 | ±0.05 | 20.17 | ±0.05 |

salt had been added to the solution.   Where the soil, nitric nitrogen and salt were added, 98.8 per cent of the nitric nitrogen was recovered.   Therefore, not one of the seventeen salts added has interfered in this method, for we find the quantity of nitric nitrogen recovered in presence of the salts, both in the pure solutions and with the soil, to be within experimental error the same as that obtained from sodium nitrate solution.

Further, the agreement among determinations is just as good as in the absence of the salt.   Moreover, these results give a fair idea of the accuracy of the method.

### INFLUENCE OF OTHER SUBSTANCES

Other substances which occur in soil and which may interfere are the soluble organic nitrogenous and non-nitrogenous constituents of soils and manure. The results obtained in the presence of a number of organic constituents are given in table 14.

Both urea and glycocoll yield their nitrogen as ammonia in the Ulsch method, but, as may be seen from the above results, this error may be obviated without a loss of nitric nitrogen by evaporating the alkaline solution to dryness before reduction. In many tests it has been our experience that when dried blood was added to the soil with a definite quantity of nitric nitrogen, slightly less than 100 per cent of the added nitric nitrogen was recovered. There can be but little doubt that this is due to the reacting of the sodium or

TABLE 14

*Nitric nitrogen obtained from various organic substances*

| TREATMENT | NITRIC NITROGEN | STANDARD DEVIATION |
|---|---|---|
| | *mgm.* | |
| 0.5 grams peptone................................. | 0.04 | ±0.17 |
| 0.5 grams asparagin (Merks)........................ | 0.09 | ±0.05 |
| 0.5 grams asparagin (Merks) + 10 mgm. nitric nitrogen | 10.02 | ±0.00 |
| 0.5 grams hippuric acid (Merks).................... | 0.07 | ±0.07 |
| 0.5 grams hippuric acid (Merks) + 10 mgm. nitric nitrogen........................................ | 9.96 | ±0.17 |
| 0.5 grams urea................................... | 55.65 | ±10.30 |
| 0.5 grams urea + 10 mgm. nitric nitrogen............ | 90.86 | ±3.43 |
| 0.5 grams urea + 10 mgm. nitric nitrogen boiled to dryness with 2 cc. NaOH......................... | 10.00 | ±0.73 |
| 10 grams dried blood + 10 mgm. nitric nitrogen...... | 8.89 | ±0.14 |
| 0.5 grams glycocoll + 10 mgm. nitric nitrogen boiled to dryness with 2 cc. NaOH......................... | 9.93 | ±0.00 |

potassium nitrate with the proteins of the added blood. If the resulting compound is insoluble, it will settle from the supernatant liquid and thus be lost; while if a soluble compound is formed, subsequent reduction will fail to liberate the nitric nitrogen. If this is the true explanation of the loss noted we can expect no better results with any of the other methods yet in use.

It is important to note in this connection that the disparate results, reported by some in nitrification experiments where large quantities of dried blood have been used, may, in a measure, be due to this loss of nitric nitrogen noted. However, it is likely that in the regular nitrification experiments, where only 1 or 2 per cent of dried blood has been added to the soil and this incubated for twenty-one days, the error would be very small.

Experiments in which various quantities of artificial humus were mixed with varying quantities of nitric nitrogen showed that this addition did not interfere with the accuracy of the test. Ulsch (52) modified his original method

by using just a little less than enough acid in the receiver to neutralize the ammonia distilled over and then titrating back the excess of ammonia with a standard acid, but we have always used an excess of acid, for Hopkins (24) has pointed out that otherwise there may be a loss of ammonia.

### SUMMARY

Clear soil extracts may be obtained by adding 2 grams of lime, ferric sulfate, ferric alum, sodium alum, or potassium alum to the soil-water mixture, by filtering through the Chamberland-Pasteur filter, or centrifuging. The last three procedures give a clear solution with a minimum loss of nitric nitrogen.

Calcium oxide added to a soil-water mixture gives a clear supernatant solution, but the quantity of nitric nitrogen obtained from such a solution is low. This is not entirely due to the mechanical removal of the nitric nitrogen with the precipitated colloid, for when calcium oxide is added to a clear sodium nitrate solution similar results are obtained.

The same quantity of nitric nitrogen was obtained from soil when the ratio of soil to water varied from as low as 1 to 5 to as high as 1 to 25.

No increase in nitric nitrogen is obtained by shaking a soil with water more than five minutes, provided the soil is well pulverized and thoroughly agitated during this time.

Very little nitric nitrogen is lost during twenty-four hours from soil-water mixtures to which 2 grams of alum or 5 grams of lime have been added, and no loss was noted from such solutions even after one hundred and sixty-eight hours when one part per thousand of chloroform had been added to the mixture. But when thymol had been added to such a solution, it accelerated the loss of nitric nitrogen.

None of the following salts interfere in the Ulsch reduction method: chlorides, sulfates, or carbonates of sodium, potassium, calcium, magnesium, manganese and iron. Hence, none of the inorganic salts which may occur in the soil interfere.

When urea or glycocoll are present, high results are obtained unless the alkaline solution is evaporated to dryness before reduction. This may be done without a loss of nitric nitrogen.

When dried blood is mixed with a nitrate less than 100 per cent of the nitric nitrogen is recovered by this method. There can be but little doubt that this is due to the reacting of nitrate with the proteins of the blood. If the resulting compound is insoluble it will settle from the supernatant liquid and thus be lost, while if soluble subsequent reduction will fail to liberate the nitric nitrogen; hence, we would find the same error entering with any of the other methods.

The aluminum reduction method, as modified by Burgess for the determination of nitric nitrogen in alkali soil, permits of an appreciable loss of nitric nitrogen. This is obviated by the use of the iron reduction method which may be outlined as follows.

One hundred grams of the finely ground soil, together with 500 cc. of distilled water, are placed in quart Mason jars and agitated for five minutes—preferably in a shaker. The solution is clarified by one of the following methods:

1. The addit on of 2 grams of alum with the soil.
2. Filtering through the Chamberland-Pasteur filter.
3. Centrifugation.

If the alum is used, no other antiseptic is necessary, but unless the analysis is to be completed at once in either of the other cases it is well to add 0.5 cc. of chloroform to each sample. An aliquot part (100 cc.) of the supernatant liquid is pipetted off, and, together with 2 cc. of a saturated solution of sodium hydroxide, evaporated to about one-fourth of its original volume to free from ammonia. If urea is present, it is necessary to evaporate to dryness. To this is added 50 cc. of ammonia-free water, 5 grams of "iron-by-hydrogen" and 30 cc. of sulfuric acid (sp. gr. 1.35). If less than 40 mgm. of nitric nitrogen is to be determined, it is well to take a correspondingly smaller quantity of iron and sulfuric acid. The neck of the reduction flask is fitted with a 2-hole stopper through which passes a 50-cc. separatory funnel and a bent tube which dips into a vessel containing water to prevent mechanical loss. The acid is slowly added and allowed to stand until the rapid evolution of hydrogen is over and then heated to boiling for ten minutes. The contents of the side vessel should be returned to the reduction flask before the reaction is complete, thus insuring the complete reduction of any nitrates which may have been carried over with the first violent evolution of the hydrogen. The contents of the reduction flask are transferred to a Kjeldahl flask, neutralized with sodium hydroxide, and distilled into standard acid. The excess of acid is titrated back with standard alkali, lacmoid being used as an indicator; checks should be made on all the reagents, including the alum used as a flocculant.

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PLATE 1

Apparatus Used in Experiment Shown in Operation
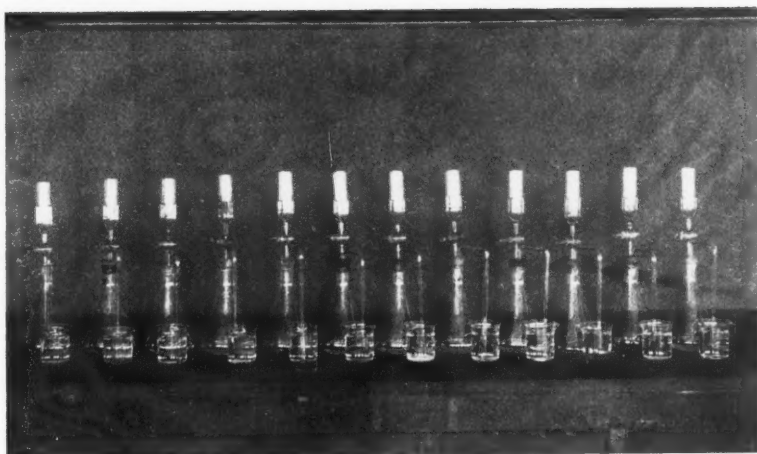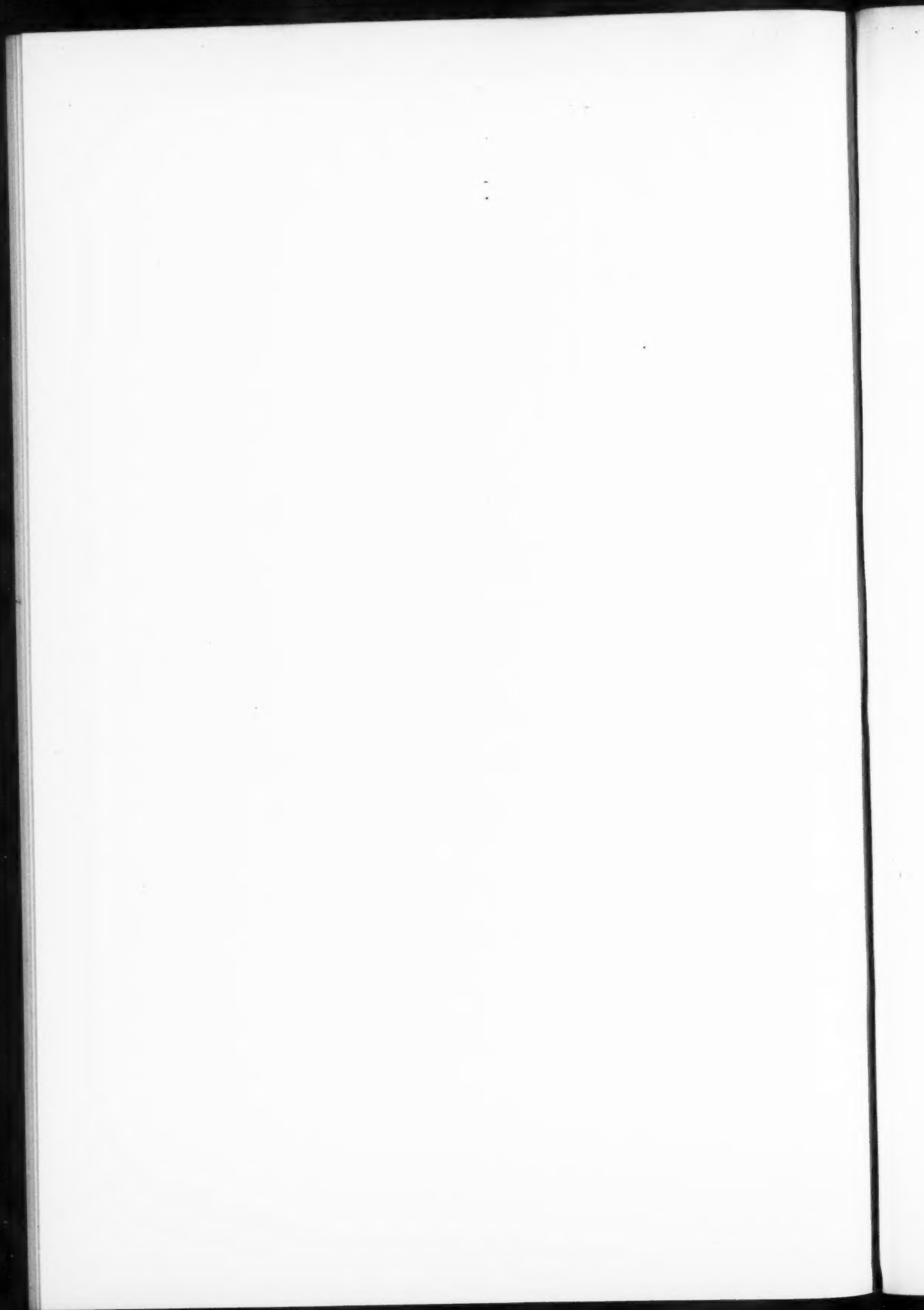
# THE EFFECTS OF ALKALI SALTS ON NITRIFICATION

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During the last few years it has been recognized that the effects of certain so-called "alkali" salts on soil bacteria, as well as their action on higher plants, should have an important bearing on the development of methods of reclamation of the alkali soils of the arid regions. It was for the purpose of throwing more light on this problem that the following experiments were carried out.

Many experiments have been conducted to determine the concentration at which various alkali salts become toxic to plants, but it remained for C. B. Lipman (8, 9, 10) to point out the importance of bacteriological studies along such lines. The investigations of this author have indicated that bacterial activities in alkali soils are very different from those in normal soils, and that the amount and character of the salts present determine the kind and extent of bacterial action occurring in such soils.

He studied the influence of sodium chloride, sodium sulfate and sodium carbonate on ammonification, nitrification and nitrogen-fixation. He found that all these processes are inhibited by the presence of certain amounts of these salts but the concentration at which each became toxic varied among the different processes. Thus the ammonifying and nitrifying bacteria were differently affected by the salts. The nitrifying bacteria were affected in a manner similar to that shown with the higher plants, but such was not the case with the ammonifying organisms. The nitrogen-fixing organisms seemed to be more resistant to injury from the salts than either of the other groups studied. The results with nitrification which are of special interest in this work showed that sodium carbonate became toxic at a concentration of 0.025 per cent, sodium sulfate at a concentration of 0.35 per cent and sodium chloride at a concentration of 0.1 per cent.

The toxic effects of salts on nitrification have been considered in few other experiments. Deherain (2, 3) noted an injurious effect of sodium chloride on nitrification and J. G. Lipman (11) found that sodium chloride became toxic at 0.1 per cent but did not entirely stop nitrification. This latter experiment was carried out by the solution method.

Headden (5, 6) and Sackett (12) have assumed the occurrence of a very intense nitrification in certain areas in Colorado to account for the excessive accumulations of nitrates occurring there, but Stewart (13) insists that such accumulations are not due to rapid *present* bacterial action, but to a concentration of the nitrates already present in the soils, the irrigation water merely furnishing a medium by which they are moved from place to place.

Furthermore, he asserts that these accumulations of nitrates always occur with large amounts of other water-soluble salts. The study of the effect of salts on nitrification may throw some light on this controversy.

Recent experiments by Kelley (7) on nitrification in semi-arid soils showed that 0.05 per cent of $Na_2CO_3$ was distinctly toxic to the nitrification of 1 per cent of dried blood, but as high a concentration as 0.4 per cent had no effect on the nitrification of 0.1 per cent of dried blood. When 0.15 per cent of ammonium sulfate was employed in the tests, 0.1 per cent of $Na_2CO_3$ became toxic to nitrification, but the same amount was markedly stimulating when 0.0625 per cent of ammonium sulfate was used. Similar results were secured with $Na_2SO_4$.

No other investigations of a nature to be of value to the general problem have been carried out so far as the authors are aware.

## EXPERIMENTAL

The purpose of the experiments reported in the following pages was to determine the concentration at which various alkali salts become toxic to the nitrifying bacteria. Alkali salts, in the concentration which was found in an alkali soil, according to chemical analysis, were added to a similar normal soil. Thus artificial alkali soils containing single salts and various combinations of the same salts were prepared. Comparative tests were run on a typical alkali soil and it was desired by this plan to ascertain the relative and absolute toxicity to the nitrifying bacteria of various salts in actual concentrations found in the field.

Alkali soil was then treated with sodium carbonate and sodium bicarbonate with and without the amount of gypsum necessary to react with the salt added in order to study nitrification under such conditions.

Samples of alkali soil and of a similar normal soil were secured through the courtesy of the Agricultural Experiment Station of the University of Wyoming, and served as a basis for the work. The tests were therefore carried out with typical alkali soil and a typical normal soil from the same region.

Chemical analyses were made of the soils and the water-soluble calcium, sodium, magnesium, potassium, bicarbonate, carbonate, chloride and sulfate determined.

The results of the analyses were as follows:

|  | NORMAL SOIL | ALKALI SOIL |
|---|---|---|
|  | *per cent* | *per cent* |
| Calcium (Ca) | 0.0220 | 0.0550 |
| Magnesium (Mg) | 0.0064 | 0.0096 |
| Sodium (Na) | 0.0796 | 0.2570 |
| Potassium (K) | 0.0218 | 0.0470 |
| Bicarbonate ($HCO_3$) | 0.0042 | 0.1190 |
| Chloride (Cl) | 0.0003 | 0.0084 |
| Sulfate ($SO_4$) | 0.0980 | 0.8330 |
| Nitrogen (Total N) | 0.1170 | 0.0440 |

The laboratory tests were carried out in tumblers with both the normal and the alkali soils according to the treatments indicated above. One-hundred-gram quantities of the air-dried, sieved soil were weighed out, salt additions made according to the various series, 100 mgm. of ammonium sulfate added, the moisture content of the soils adjusted to the optimum, 5 cc. of a five-minute infusion of a fresh soil added to each soil to introduce a vigorous nitrifying flora, the tumblers were then covered and incubated for four weeks at room temperature, the moisture content being kept up by additions of sterile water to weight every ten days. The nitrates present were then determined by the aluminum reduction method, modified somewhat from the procedure recommended by Burgess (1).

### Series I. The effects of NaCl on nitrification in normal soil

The arrangement of this series and the results are shown in table 1 and figure 1. All the treatments were in duplicate and the untreated normal soil and

TABLE 1

*Effects of NaCl on nitrification in normal soil*

| NUMBER | SOIL | NaCl | N | AVERAGE N |
|--------|------|------|---|-----------|
| | | grams | mgm. | mgm. |
| 1 | Normal | None | 2.1728 | |
| 2 | Normal | None | 2.2316 | 2.2022 |
| 3 | Normal | 0.005 | 3.1164 | |
| 4 | Normal | 0.005 | 3.2460 | 3.1812 |
| 5 | Normal | 0.010 | 2.2316 | |
| 6 | Normal | 0.010 | 2.5452 | 2.3884 |
| 7 | Normal | 0.020 | 2.0328 | |
| 8 | Normal | 0.020 | 1.7164 | 1.8746 |
| 9 | Normal | 0.040 | 0.6608 | |
| 10 | Normal | 0.040 | 0.9464 | 0.8536 |
| 11 | Alkali | None | 2.0888 | |
| 12 | Alkali | None | 1.8312 | 1.9600 |

untreated alkali soil were used in this and all succeeding series for the sake of comparison.

The addition of 0.005 per cent of NaCl gave a stimulation in nitrate production but the large amounts, at least beyond 0.010 per cent depressed nitrification. This latter amount apparently had no effect.

The alkali soil gave a smaller nitrification than the normal soil and about the same as that receiving 0.020 per cent of NaCl. The toxic point for the NaCl in this test evidently occurred at about 0.02 per cent, which is very much lower than the concentration at which Lipman found toxicity. Differences in the soils tested may account for the variation in the results. It is apparent, however, that small amounts of NaCl stimulate nitrification, while larger amounts bring about a depression.
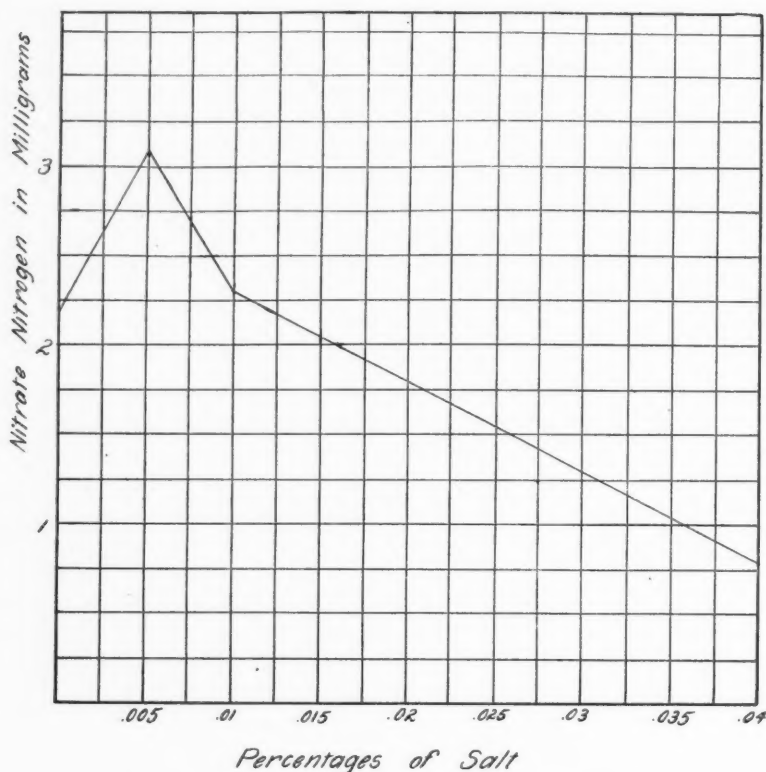
FIG. 1. EFFECTS OF NaCl ON NITRIFICATION IN NORMAL SOIL

*Series II. The effects of Na₂SO₄ on nitrification in normal soil*

This series was arranged in a manner similar to the preceding except that the treatments with Na₂SO₄ were much larger than those with NaCl. The data obtained are presented in table 2 and figure 2.

The addition of the Na₂SO₄ up to 2.0720 per cent increased considerably the nitrifying power of the soil. The greatest increase was secured with 0.5180 per cent of the salt, but the differences between the results with this application and with the larger amounts were small until 4.1440 per cent was added, when a distinct depression in nitrification occurred. The concentration at which the sodium sulfate becomes toxic was therefore much higher in this soil than in Lipman's experiments, where the toxic point was found to be 0.35 per cent. The variation in the soil used would again probably explain the difference in the results. It is evident again, however, that sodium

TABLE 2

*Effects of Na₂SO₄ on nitrification in normal soil*

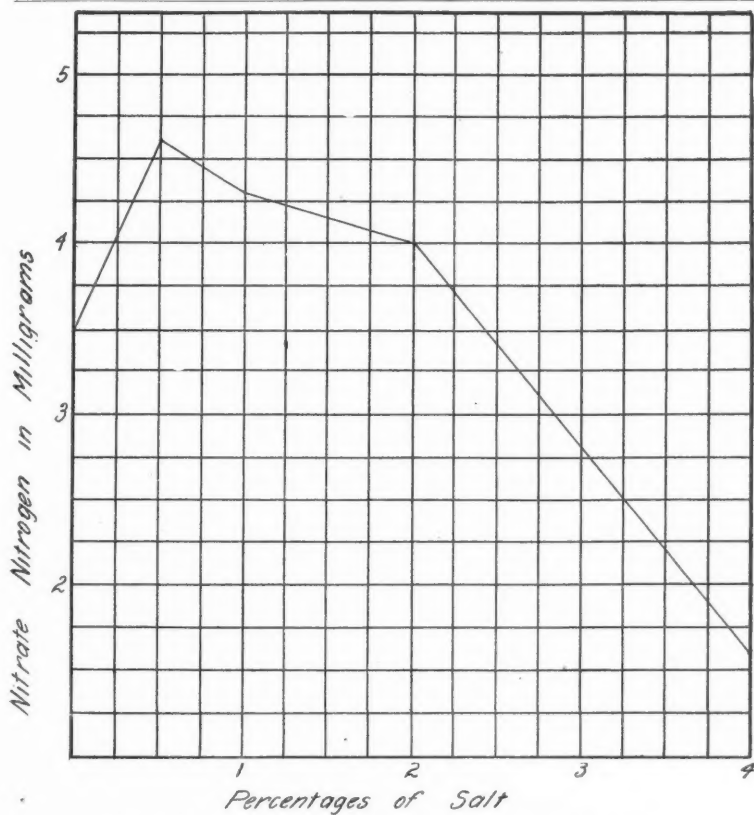| NUMBER | SOIL | Na₂SO₄ | N | AVERAGE N |
|--------|------|--------|---|-----------|
| | | grams | mgm. | mgm. |
| 1 | Normal | None | 3.3150 | |
| 2 | Normal | None | 3.6960 | 3.5030 |
| 3 | Normal | 0.5180 | 4.6280 | |
| 4 | Normal | 0.5180 | Lost | 4.6280 |
| 5 | Normal | 1.0360 | 4.4570 | |
| 6 | Normal | 1.0360 | 4.3140 | 4.3850 |
| 7 | Normal | 2.0720 | 4.1740 | |
| 8 | Normal | 2.0720 | 3.8860 | 4.0290 |
| 9 | Normal | 4.1440 | 1.6010 | |
| 10 | Normal | 4.1440 | 1.7750 | 1.6880 |
| 11 | Alkali | None | 3.1720 | |
| 12 | Alkali | None | 2.9450 | 3.0580 |



FIG. 2. EFFECTS OF Na₂SO₄ ON NITRIFICATION IN NORMAL SOIL

sulfate stimulates nitrification when added in small amounts, but when the concentration is increased beyond a certain point, which varies in different soils, it becomes distinctly toxic to the nitrifiers.

*Series III. The effects of* $MgSO_4$ *on nitrification in normal soil*

The arrangement of this series and the results secured appear in table 3 and figure 3.

TABLE 3

*Effects of* $MgSO_4$ *on nitrification in normal soil*

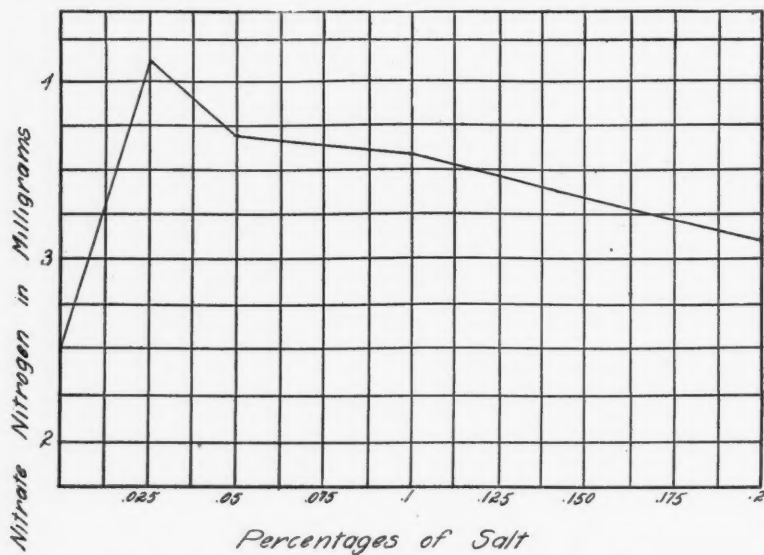| NUMBER | SOIL | $MgSO_4$ | N | AVERAGE N |
|:---:|:---:|:---:|:---:|:---:|
| | | grams | mgm. | mgm. |
| 1 | Normal | None | 2.5375 | |
| 2 | Normal | None | 2.4841 | 2.5108 |
| 3 | Normal | 0.0235 | 4.0984 | |
| 4 | Normal | 0.0235 | 4.2998 | 4.1991 |
| 5 | Normal | 0.0570 | 3.4020 | |
| 6 | Normal | 0.0570 | 4.0292 | 3.7156 |
| 7 | Normal | 0.1140 | 3.6008 | |
| 8 | Normal | 0.1140 | 3.6306 | 3.6162 |
| 9 | Normal | 0.2280 | 3.1724 | |
| 10 | Normal | 0.2280 | 3.0604 | 3.1164 |
| 11 | Alkali | None | 2.0964 | |
| 12 | Alkali | None | 2.0952 | 2.0976 |



FIG. 3. EFFECTS OF $MgSO_4$ ON NITRIFICATION IN NORMAL SOIL
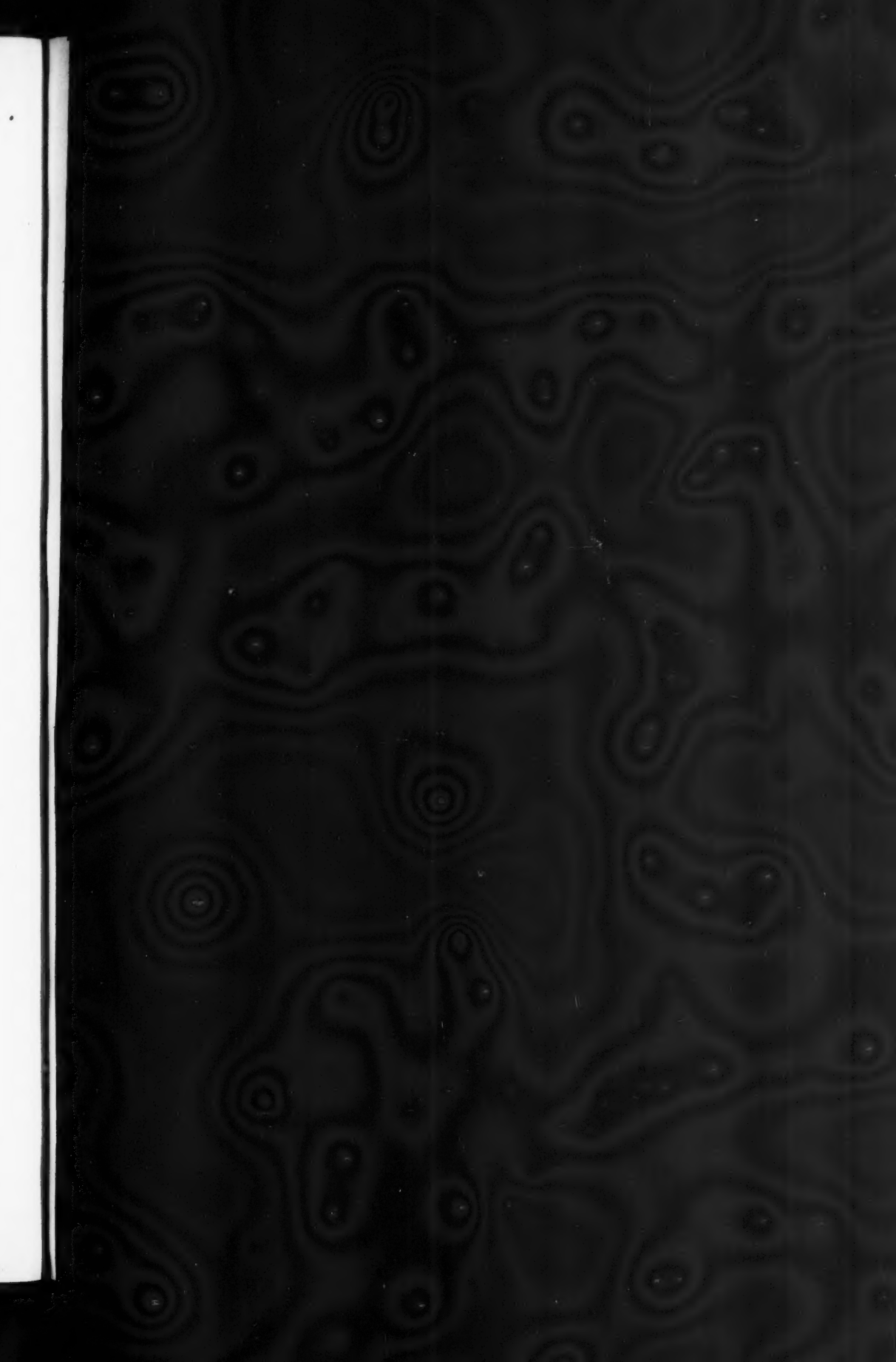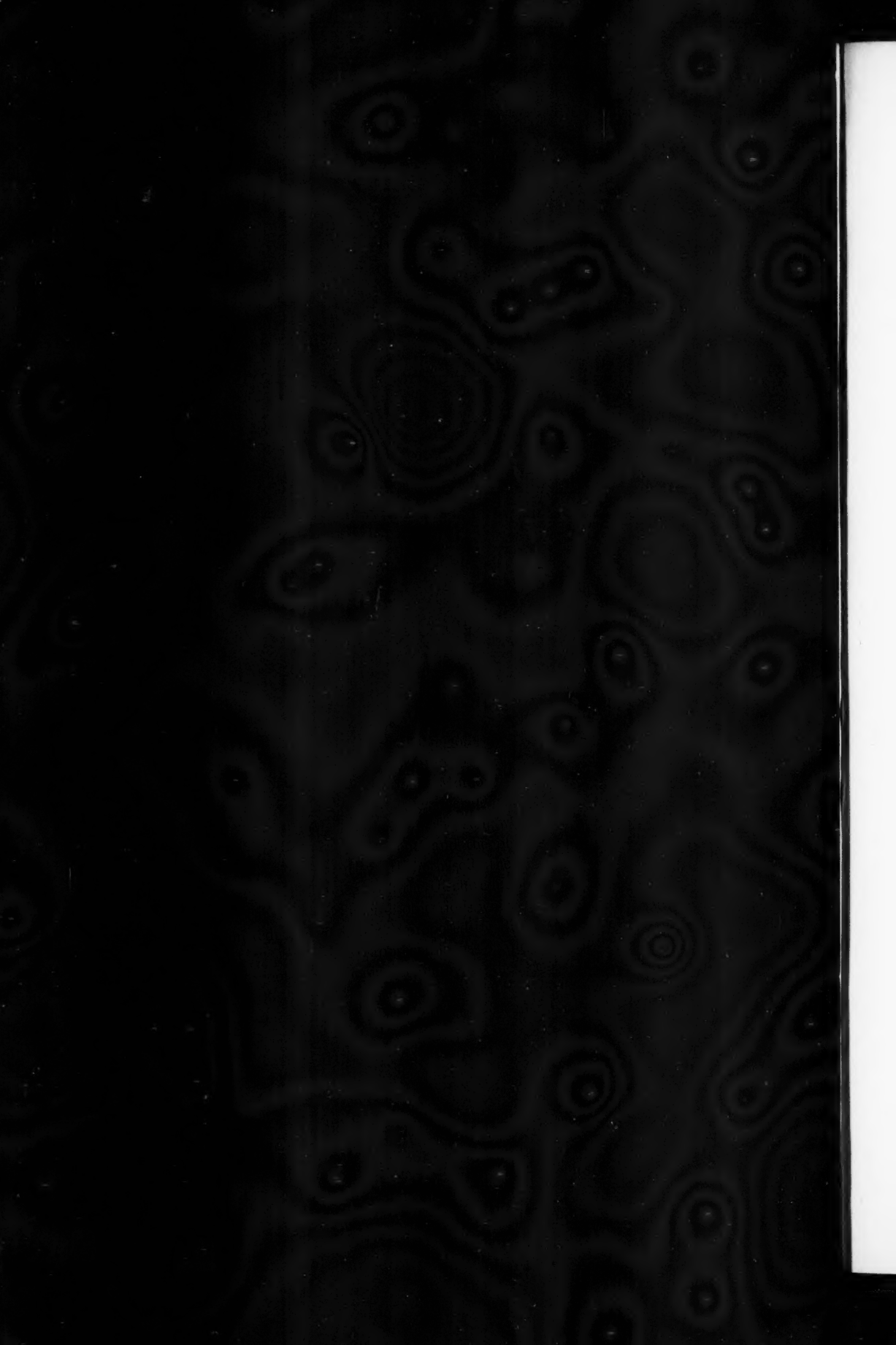
The MgSO$_4$ evidently stimulated nitrification in all the amounts used, that is, up to 0.2280 per cent. The greatest stimulation occurred, however, with the smallest appliction—0.0235 per cent, and the larger amounts brought about smaller effects. If the application had been increased beyond 0.2280 per cent it seems that a depression in nitrification would have occurred, for the figures gradually decreased with increasing applications. Just where a toxic effect from the MgSO$_4$ would occur, cannot, of course, be stated from these results, but it is probable that about 0.3 per cent would mark the point at which depression would occur.

Again it is seen that this salt, like the others tested, stimulates nitrification when present in small amounts, but beyond a certain maximum concentration undoubtedly becomes toxic.

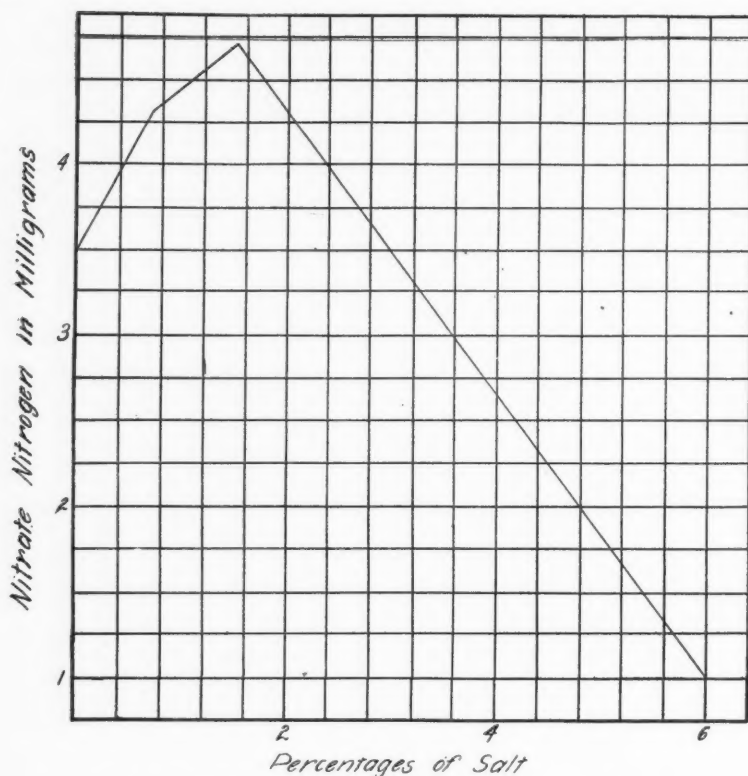### Series IV. The effects of CaCO$_3$ on nitrification in normal soil

The effects of calcium carbonate upon crops and soils have commonly been found to be beneficial, with but few exceptions. It might be expected, therefore, that the nitrifying bacteria would be stimulated in action by additions of this salt.

Examining the results of this series in table 4 and figure 4, it will be seen that a stimulation in nitrification occurred when calcium carbonate was ap-

TABLE 4

*Effects of CaCO$_3$ on nitrification in normal soil*

| NUMBER | SOIL | CaCO$_3$ | N | AVERAGE N |
|--------|------|----------|-----|-----------|
|        |      | grams    | mgm. | mgm.     |
| 1      | Normal | None   | 3.5168 |         |
| 2      | Normal | None   | 3.5364 | 3.5266  |
| 3      | Normal | 0.189  | 3.5978 |         |
| 4      | Normal | 0.189  | 3.6700 | 3.6339  |
| 5      | Normal | 0.378  | 3.8444 |         |
| 6      | Normal | 0.378  | 3.9452 | 3.8948  |
| 7      | Normal | 0.756  | 4.2728 |         |
| 8      | Normal | 0.756  | 4.3736 | 4.3232  |
| 9      | Normal | 1.512  | 4.7432 |         |
| 10     | Normal | 1.512  | 4.7824 | 4.7628  |
| 11     | Normal | 6.048  | 1.1340 |         |
| 12     | Normal | 6.048  | 1.0612 | 1.0976  |

plied up to a treatment of 6 per cent. Somewhere between 1.512 per cent and 6.048 per cent occurred the toxic point for this salt on this particular soil. Unfortunately, the exact point was not ascertained. It is of considerable interest to note, however, the undoubted toxicity to nitrification indicated by the application of 6.048 per cent. Evidently calcium carbonate in small or reasonable amounts is beneficial to nitrification, but when the addition becomes excessive there is a depression in the activities of this group of or-

FIG. 4. EFFECTS OF CaCO₃ ON NITRIFICATION IN NORMAL SOIL

ganisms. This depression may not occur in other soils, but these results on one particular soil indicate that calcium carbonate may be applied to soils in too large amounts.

*Series V. The effects of* NaHCO₃ *on nitrification in alkali soil*

This series deals with the effects of sodium bicarbonate on nitrification in an alkali soil. The treatment of the soil and the results appear in table 5 and figure 5. Examining the table, it is seen that the NaHCO₃ in additions up to and beyond 0.10 per cent stimulated considerably the nitrification process in this soil. Beyond 0.30 per cent, however, a distinct depression occurred which increased with increasing additions.

When calcium sulfate was added with the sodium bicarbonate, all toxic effects of the additions were removed, as is indicated by the results of the last two tests in the table.

TABLE 5

*Effects of NaHCO₃ on nitrification in alkali soil*

| NUMBER | SOIL | NaHCO₃ | N | AVERAGE N |
|---|---|---|---|---|
| | | grams | mgm. | mgm. |
| 1 | Alkali | None | 4.6172 | |
| 2 | Alkali | None | 4.5416 | 4.5794 |
| 3 | Alkali | 0.05 | 4.8740 | |
| 4 | Alkali | 0.05 | 4.7650 | 4.8190 |
| 5 | Alkali | 0.10 | 5.4740 | |
| 6 | Alkali | 0.10 | 5.3228 | 5.3984 |
| 7 | Alkali | 0.30 | 3.8864 | |
| 8 | Alkali | 0.30 | 4.2148 | 4.0506 |
| 9 | Alkali | 0.50 | 3.8360 | |
| 10 | Alkali | 0.50 | 3.9116 | 3.8738 |
| 11 | Alkali | 1.00 | 3.7604 | |
| 12 | Alkali | 1.00 | 3.1808 | 3.4706 |
| 13* | Alkali | 1.00 | 4.9448 | |
| 14* | Alkali | 1.00 | 4.8440 | 4.8944 |

* Plus 1.6197 grams CaSO₄.

Sodium bicarbonate appears, from these results, to have a stimulative effect on nitrification when added to soil to 0.10 to 0.30 per cent, but it becomes toxic to the process when applied at the rate of 0.30 per cent and beyond, the toxicity increasing with the addition.
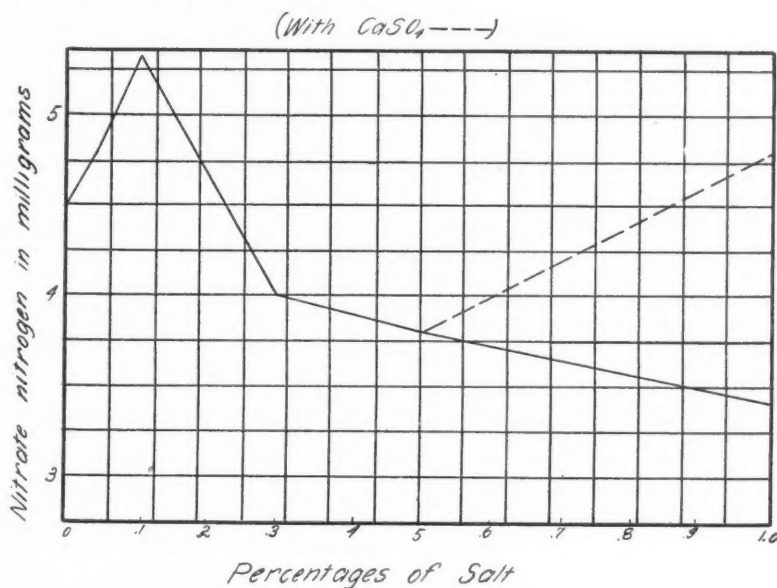


FIG. 5. EFFECTS OF NaHCO₃ ON NITRIFICATION IN ALKALI SOIL

When calcium sulfate is added with the sodium bicarbonate in the proper amount to react with this latter salt, all toxic effect is removed and there is apparently no influence from the addition, except perhaps a slight increase in the nitrification process.

### Series VI. The effects of $Na_2CO_3$ on nitrification in alkali soil

The arrangement of this series was very similar to the preceding. It is shown in table 6 and figure 6 together with the results.

TABLE 6

*Effects of $Na_2CO_3$ on nitrification in alkali soil*

| NUMBER | SOIL | $Na_2CO_2$ | N | AVERAGE N |
|--------|------|-----------|-----|-----------|
| | | grams | mgm. | mgm. |
| 1 | Alkali | None | 2.1476 | |
| 2 | Alkali | None | 1.7948 | 1.9712 |
| 3 | Alkali | 0.05 | 3.1528 | |
| 4 | Alkali | 0.05 | 1.8480 | 2.5004 |
| 5 | Alkali | 0.10 | 1.6436 | |
| 6 | Alkali | 0.10 | 2.5256 | 2.0846 |
| 7 | Alkali | 0.30 | 2.2484 | |
| 8 | Alkali | 0.30 | 1.6184 | 1.9334 |
| 9 | Alkali | 0.50 | 1.9936 | |
| 10 | Alkali | 0.50 | 1.5176 | 1.7556 |
| 11 | Alkali | 1.00 | 1.2656 | |
| 12 | Alkali | 1.00 | 1.7416 | 1.5036 |
| 13* | Alkali | 1.00 | 2.1252 | |
| 14* | Alkali | 1.00 | 1.8480 | 1.9866 |

* Plus 1.30 grams $CaSO_4$.
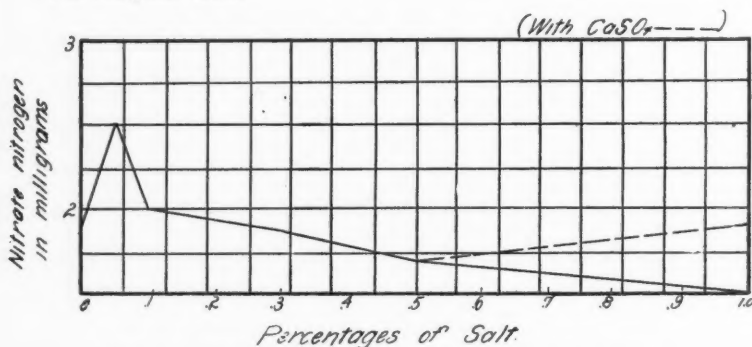


FIG. 6. EFFECTS OF $Na_2CO_3$ ON NITRIFICATION IN ALKALI SOIL

The application of the sodium carbonate at the rate of 0.05 per cent gave a decided stimulation in nitrification. The 0.10 per cent addition, likewise, gave a stimulation, but it was not large. The larger additions brought about

depressions in the process which became greater as the size of the application increased.   When calcium sulfate was added in the proper amount to react with the sodium carbonate there was no effect whatever from the addition. This result is in accord with that of the preceding series with the bicarbonate of sodium and the calcium sulfate.

The concentration at which the sodium carbonate became toxic to the nitrifiers in this soil was much greater than that noted by Lipman.   He found toxicity at 0.025 per cent, but stimulation occurred in this work up to 0.10 per cent.   His results with $Na_2CO_3$, however, were not considered satisfactory, as there was much mold growth on the soils which may have used up the nitrates produced, and losses may have occurred in the several filtrations through bone black which were necessary to the determination.   However, the variation from Lipman's results may be due, as was concluded in the preceding series, to differences in the soil used.   It is evident, however, that sodium carbonate, like the other salts tested, stimulated nitrification when used in small amounts, but depressed the process considerably when large applications were made.   When calcium sulfate is used with the sodium carbonate, there is no effect on the nitrifying bacteria.

### Series VII. The effects of $CaSO_4$ on nitrification in alkali soil

The results in the preceding tables indicated that calcium sulfate applied with sodium carbonate and sodium bicarbonate neutralized the toxic effects

TABLE 7

*Effects of $CaSO_4$ on nitrification in alkali soil*

| NUMBER | SOIL | $CaSO_4$ | N | AVERAGE N |
|--------|------|------|------|------|
| | | grams | mgm. | mgm. |
| 1 | Alkali | None | 4.1804 | |
| 2 | Alkali | None | 4.3120 | 4.2462 |
| 3 | Alkali | 0.022 | 4.4156 | |
| 4 | Alkali | 0.022 | 4.4436 | 4.4298 |
| 5 | Alkali | 0.033 | 4.4436 | |
| 6 | Alkali | 0.033 | 4.5752 | 4.4894 |
| 7 | Alkali | 0.044 | 4.5472 | |
| 8 | Alkali | 0.044 | 4.6284 | 4.5878 |
| 9 | Alkali | 0.088 | 4.4156 | |
| 10 | Alkali | 0.088 | 4.3120 | 4.3638 |
| 11 | Alkali | 0.176 | 4.1664 | |
| 12 | Alkali | 0.176 | 4.3904 | 4.2784 |

of these salts.   It seemed advisable, therefore, to ascertain the influence of the $CaSO_4$ when applied alone to the alkali soil.   The treatments used and the results secured appear in table 7 and figure 7.

It is apparent upon an examination of this table that the $CaSO_4$ had little effect on nitrification.   There seemed to be a slight stimulation with the

smaller additions, but the differences were not large.    With the larger amounts, no increase was secured.    The applications were not increased beyond 0.176 per cent, so it is quite possible that further additions might have brought about an increase in nitrification.    However, in the absence of suffiicent data, general conclusions cannot be drawn.    The differences secured seem too small to conclude a stimulation of the process, but the results may be considered to indicate the possibility of such a stimulation at least.
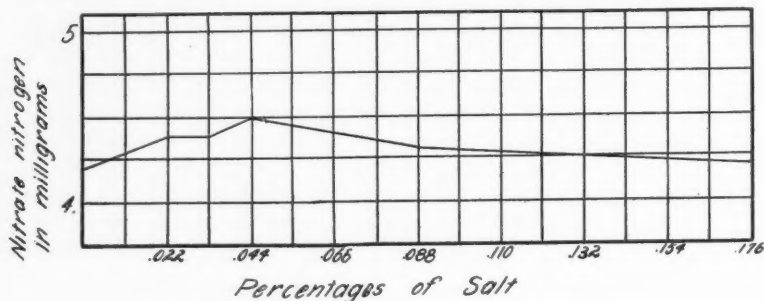


FIG. 7. EFFECTS OF CaSO₄ ON NITRIFICATION IN ALKALI SOIL

*Series VIII. The effects of CaCO₃ on nitrification in alkali soil*

When calcium carbonate was applied to the normal soil used in this work, a distinct stimulation of nitrification occurred up to 6.0 per cent.  At that point, however, the activities of the nitrifiers were quite considerably depressed. It seemed desirable, therefore, to test the effects of that salt on nitrification in the alkali soil.

This series was arranged in a similar manner to series IV except that the alkali soil was used.    The arrangement of the series and the results are given in table 8 and figure 8.

The small amounts of the CaCO₃ did not seem to influence nitrification, but when 0.378 per cent was used an increase in the process was noted.    Further gains occurred with the larger applications up through 1.512 per cent.    When 6.046 per cent was added, however, a distinct depression in nitrification occurred.    Evidently the maximum increase in the process through the use of CaCO₃ on this soil occurred at 1.512 per cent, or between that amount and 6.048 per cent.

The absence of tests using intermediate amounts prevents any definite point being established.    It is evident, however, that just as was the case in the tests with the normal soil, CaCO₃ when applied in small amounts to this alkali soil increased nitrification, but when 6.048 per cent was used, a decided depression in the process occurred.    Such an amount of CaCO₃ is rarely found in soil and hence, even if an injurious effect were found to be quite general (with many soils), which is extremely unlikely, no danger from a *reasonable* use of lime on soils need be apprehended.

TABLE 8

*Effects of CaCO₃ on nitrification in alkali soil*

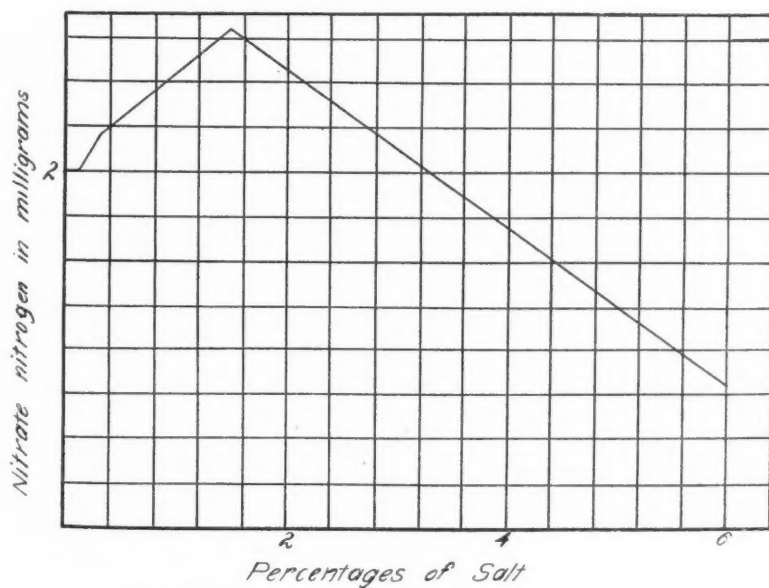| NUMBER | SOIL | CaCO₃ | N | AVERAGE N |
|--------|------|-------|-----|-----------|
| | | grams | mgm. | mgm. |
| 1 | Alkali | None | 2.1586 | |
| 2 | Alkali | None | 1.8900 | 2.0243 |
| 3 | Alkali | 0.189 | 2.0188 | |
| 4 | Alkali | 0.189 | 2.0440 | 2.0314 |
| 5 | Alkali | 0.378 | 2.1700 | |
| 6 | Alkali | 0.378 | 2.2960 | 2.2330 |
| 7 | Alkali | 0.756 | 2.3960 | |
| 8 | Alkali | 0.756 | 2.4976 | 2.4468 |
| 9 | Alkali | 1.512 | 2.7134 | |
| 10 | Alkali | 1.512 | 2.9026 | 2.8080 |
| 11 | Alkali | 6.048 | 1.0108 | |
| 12 | Alkali | 6.048 | 0.7840 | 0.8974 |



FIG. 8. EFFECTS OF CaCO₃ ON NITRIFICATION IN ALKALI SOIL

*Series IX. The effects of* $NaHCO_3$, $Na_2CO_3$ *and* $CaSO_4$ *on nitrification in alkali soil*

This series was planned to test the effect of the carbonate and bicarbonate of sodium on nitrification in alkali soil in the presence of calcium carbonate and with and without the addition of sufficient calcium sulfate to react with the carbonate used. The arrangement of the tests and the results secured are given in table 9 and figure 9.

TABLE 9

*Effects of* $NaHCO_3$, $Na_2CO_3$, *and* $CaSO_4$ *on nitrification in the presence of* $CaCO_3$ *in alkali soil*

| NUMBER | ADDITION | N | AVERAGE N |
|---|---|---|---|
| | | *mgm.* | *mgm.* |
| 1 | Nothing.................................................. | 2.3296 | |
| 2 | Nothing.................................................. | 2.5312 | 2.4304 |
| 3 | 0.536 gram $CaCO_3$....................................... | 2.9960 | |
| 4 | 0.536 gram $CaCO_3$....................................... | 4.1440 | 3.5700 |
| 5 | 0.536 gram $CaCO_3$ + 1.00 gram $NaHCO_3$ ................. | 2.6852 | |
| 6 | 0.536 gram $CaCO_3$ + 1.00 gram $NaHCO_3$.................. | 2.5760 | 2.6306 |
| 7 | 0.536 gram $CaCO_3$ + 0.044 gram $NaHCO_3$ + 0.072 gram $CaSO_4$....................................................... | 2.4640 | |
| 8 | 0.536 gram $CaCO_3$ + 0.044 gram $NaHCO_3$ + 0.072 gram $CaSO_4$....................................................... | 2.9688 | 2.7164 |
| 9 | 0.536 gram $CaCO_3$ + 0.044 gram $NaHCO_3$.................. | Lost | |
| 10 | 0.536 gram $CaCO_3$ + 0.044 gram $NaHCO_3$.................. | 3.0016 | 3.0016 |
| 11 | 0.536 gram $CaCO_3$ + 0.056 gram $Na_2CO_3$.................. | 2.7104 | |
| 12 | 0.536 gram $CaCO_3$ + 0.056 gram $Na_2CO_3$.................. | 2.7552 | 2.7328 |
| 13 | 0.536 gram $CaCO_3$ + 0.056 gram $Na_2CO_3$ + 0.072 gram $CaSO_4$....................................................... | 3.0912 | |
| 14 | 0.536 gram $CaCO_3$ + 0.056 gram $Na_2CO_3$ + 0.072 gram $CaSO_4$....................................................... | 4.2928 | 3.6920 |
| 15 | 0.536 gram $CaCO_3$ + 1.00 gram $Na_2CO_3$.................. | 2.8224 | |
| 16 | 0.536 gram $CaCO_3$ + 1.00 gram $Na_2CO_3$.................. | Lost | 2.8224 |
| 17 | 0.536 gram $CaCO_3$ + 0.056 gram $Na_2CO_3$ + 0.044 gram $NaHCO_3$....................................................... | 2.5760 | |
| 18 | 0.536 gram $CaCO_3$ + 0.056 gram $Na_2CO_3$ + 0.044 gram $NaHCO_3$....................................................... | 3.4272 | 3.0016 |

On examining this table it is apparent that calcium carbonate increased the nitrification process to a considerable extent. This is in accord with the tests previously discussed with calcium carbonate. The sodium carbonate and the bicarbonate both depressed considerably the activities of the nitrifiers over calcium carbonate alone, the larger application bringing about a greater depression in the case of the bicarbonate, but practically the same results being secured with both amounts in the case of the carbonate.

Some differences are evident here from the results secured with the use of the two salts without calcium carbonate. In those cases the small amount

of the carbonates increased nitrification slightly, but in the presence of $CaCO_3$ in this series, a depression occurred. This is an interesting difference and points to the fact that amounts of these salts which alone are non-toxic may become toxic when present with $CaCO_3$.

When calcium sulfate was used with the smaller amount of the sodium carbonate, the injurious effect of the carbonate was neutralized and no influence on nitrification is noted. This is in accord with the results secured with the two salts in the absence of $CaCO_3$. When the bicarbonate is considered, however, the use of the calcium sulfate with the bicarbonate depressed the process more than was the case with the bicarbonate alone. This is exactly opposite from the results secured in the previous series in the ab-
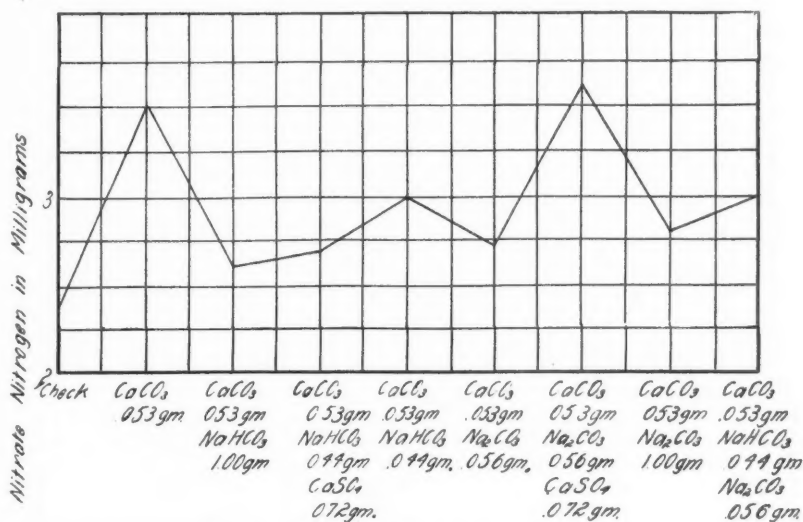


FIG. 9. EFFECTS OF $CaCO_3$ AND $NaHCO_3$, $Na_2CO_3$ AND $CaSO_4$ IN THE PRESENCE OF $CaCO_3$ ON NITRIFICATION IN ALKALI SOIL

sence of $CaCO_3$. Only one determination was made with the use of the bicarbonate alone, and hence that result may not be absolutely accurate, but the differences secured are definite enough so that it must be concluded that in the presence of $CaCO_3$ calcium sulfate does not neutralize the toxic effect of sodium bicarbonate.

When the bicarbonate and carbonate of sodium were applied together, the depression in nitrification was less than with the sodium carbonate alone and about the same as that from the bicarbonate alone.

These results, as a whole, show distinctly the toxic effects of the carbonate and bicarbonate of sodium on nitrification in this soil in the presence of $CaCO_3$. Furthermore, smaller amounts became toxic than in the same soil

in the absence of $CaCO_3$. $CaSO_4$ prevents the toxic action of sodium carbonate, but it does not seem to be similarly efficient with the bicarbonate in the presence of $CaCO_3$.

### GREENHOUSE EXPERIMENTS

Comparative experiments similar to the above were carried out in the greenhouse, nitrification tests being run on both the normal and alkali soils, after beans had been grown and harvested. In these pot experiments 10 pounds of soil were used and the treatment of the normal soil was calculated to imitate alkali-soil conditions. The amounts of the various alkali salts added singly or in combination to the normal soil were the same as those found

TABLE 10

*Effects of* NaCl, $Na_2SO_4$, $MgSO_4$ *and* $CaSO_4$ *on nitrification in normal soil*

| NUM-BER | TREATMENT | FIRST SAMPLING | | SECOND SAMPLING | | THIRD SAMPLING | |
|---|---|---|---|---|---|---|---|
| | | Average N | Average N for pots | Average N | Average N for pots | Average N | Average N for pots |
| | | *mgm.* | *mgm.* | *mgm.* | *mgm.* | *mgm.* | *mgm.* |
| 1 | None.................. | 6.6570 | | 6.6010 | | 6.9060 | |
| 2 | None.................. | 6.2748 | 6.4659 | 6.2916 | 6.4463 | 6.7088 | 6.8074 |
| 3 | 0.005 per cent NaCl..... | 6.1562 | | 6.5464 | | 7.0280 | |
| 4 | 0.005 per cent NaCl..... | 6.0088 | 6.0825 | 6.5874 | 6.5664 | 7.0168 | 7.0224 |
| 5 | 0.518 per cent $Na_2SO_4$.... | 6.5562 | | 6.5996 | | 6.3168 | |
| 6 | 0.518 per cent $Na_2SO_4$.... | 5.9066 | 6.2314 | 6.3476 | 6.4736 | 6.4932 | 6.4050 |
| 7 | 0.023 per cent $MgSO_4$.... | 7.4466 | | 5.8660 | | 6.8368 | |
| 8 | 0.023 per cent $MgSO_4$.... | 6.5940 | 7.0203 | 6.4381 | 6.1520 | 6.9622 | 6.8995 |
| 9 | 0.189 per cent $CaCO_3$..... | 6.4932 | | 6.6280 | | 7.7420 | |
| 10 | 0.189 per cent $CaCO_3$..... | 7.3234 | 7.1583 | 6.7340 | 6.6810 | 6.6870 | 7.2145 |
| 11 | All four salts............ | 6.4288 | | 6.4932 | | 6.8152 | |
| 12 | All four salts............ | 6.5940 | 6.5114 | 6.1278 | 6.3105 | 7.0158 | 6.9155 |

by analysis in the alkali soil. The alkali soil received additions of calcium carbonate and of sodium carbonate and bicarbonate with and without additions of calcium sulfate.

All the treatments were in duplicate, and the arrangement of the pots is shown in tables 10 and 11.

The pots were weighed at the time of filling and brought up to the optimum moisture content, which was 20.0 per cent for the normal soil and 20.8 per cent for the alkali soil. The moisture content was kept constant throughout the experiment by adding water to weight. This water was added by means of a tube at the bottom of the pots, in order to prevent puddling. The experiment was started on November 12, 1915, and beans seeded in all the pots in the attempt to ascertain whether the effects of the alkali salts would be the same on the crop grown as on the nitrifying organisms. After the crop was removed, samples were drawn and tested for nitrifying power on February

23, March 10 and March 20 for the normal soils, and on February 6, February 25, March 12 and March 22 for the alkali soils.   The procedure in these tests was the same as that already outlined, except that fresh soil was used, no soil infusion was added, and of course, no salts were used, the idea being to determine the nitrifying power of the soils receiving the various salts *after* a crop had been grown and *after* the salts had been present in the soil for a comparatively long period.

The results of the tests of the normal soils are given in table 10 and figures 10 and 11, and of the alkali soils in table 11 and figures 12 and 13.
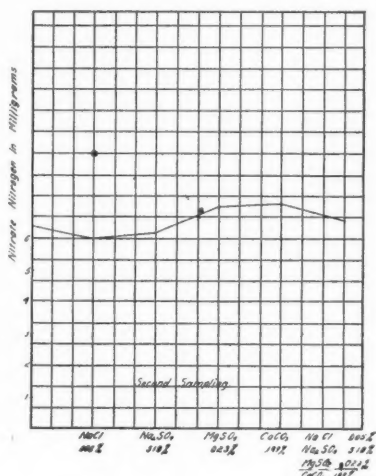


FIG. 10                              FIG. 11

FIG. 10. EFFECTS OF NaCl, Na₂SO₄, MgSO₄ AND CaCO₃ ON NITRIFICATION IN NORMAL SOIL—SECOND SAMPLING (POT EXPERIMENTS)
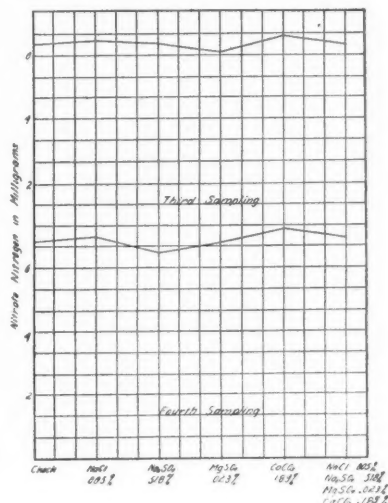
FIG. 11. EFFECTS OF NaCl, Na₂SO₄, MgSO₄, AND CaCO₃ ON NITRIFICATION IN NORMAL SOIL—THIRD AND FOURTH SAMPLINGS (POT EXPERIMENTS)

### Normal soil tests

Considering the results as a whole, it is apparent from table 10 that sodium chloride gave a very slight increase in nitrification.   This increase was quite noticeable at the last two samplings.   This effect of the use of 0.005 per cent of NaCl checks exactly with the results secured in the laboratory test with the use of NaCl as shown in table 1.   Evidently the stimulative effect of the NaCl on nitrification when amounts not exceeding 0.005 per cent were used continues for some time after the application is made, if these results in the pots are considered sufficiently definite to warrant conclusions.  At any rate, no toxic effect is seen.   Na₂SO₄ gave a slight toxic effect on the nitrifying power of the soil, as shown at the first and last samplings.   A very slight increase

TABLE 11

*Effects of CaCO₃, NaHCO₃, Na₂CO₃ and CaSO₄ on nitrification in alkali soil*

| NUMBER | TREATMENT | FIRST SAMPLING | | SECOND SAMPLING | | THIRD SAMPLING | | FOURTH SAMPLING | |
|---|---|---|---|---|---|---|---|---|---|
| | | Average N | Average N for pots | Average N | Average N for pots | Average N | Average N for pots | Average N | Average N for pots |
| | | mgm. | mgm. | mgm. | mgm. | mgm. | mgm. | mgm. | mgm. |
| 1 | None | 4.1370 | | 4.6844 | | 4.5150 | | 5.4955 | |
| 2 | None | 4.0614 | 4.0992 | 4.8454 | 4.7149 | 4.7264 | 4.6207 | 5.2106 | 5.3531 |
| 3 | 0.189 per cent CaCO₃ | 5.4642 | | 4.9784 | | 4.5262 | | 5.4950 | |
| 4 | 0.189 per cent CaCO₃ | 5.6014 | 5.5328 | 4.6592 | 4.8183 | 4.5703 | 4.5482 | 5.4418 | 5.4684 |
| 5 | 0.378 per cent CaCO₃ | Lost | | 4.7348 | | 4.7454 | | 5.8422 | |
| 6 | 0.378 per cent CaCO₃ | 5.5384 | 5.5384 | 5.8954 | 5.3151 | 5.1310 | 4.9382 | 5.3998 | 5.6210 |
| 7 | 0.109 per cent NaHCO₃ | 4.8174 | | 5.0414 | | 4.9560 | | 5.9528 | |
| 8 | 0.109 per cent NaHCO₃ | 4.6601 | 4.7384 | 5.2696 | 5.0435 | 4.4716 | 4.7138 | 4.9518 | 5.4523 |
| 9 | 0.218 per cent Na₂CO₃ | 4.9518 | | 4.9261 | | 4.5402 | | 5.9010 | |
| 10 | 0.218 per cent Na₂CO₃ | 4.8622 | 4.9070 | 6.1726 | 5.5493 | 4.8342 | 4.6872 | 5.7512 | 5.8261 |
| 11* | 0.109 per cent NaHCO₃ | 4.9644 | | 6.0970 | | 4.8384 | | 5.7512 | |
| 12* | 0.109 per cent NaHCO₃ | 4.7710 | 4.8677 | 6.0088 | 6.0529 | 4.8230 | 4.8307 | 6.2216 | 5.9864 |
| 13† | 0.218 per cent Na₂CO₃ | Lost | | 5.6168 | | 4.9560 | | 7.0424 | |
| 14† | 0.218 per cent Na₂CO₃ | 5.5916 | 5.5916 | 6.5170 | 6.0669 | 5.1310 | 5.0440 | 6.5324 | 6.7874 |

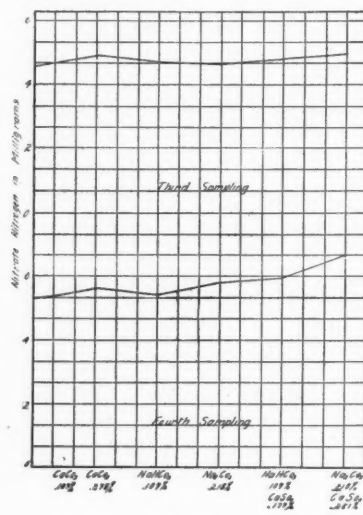\* Plus 0.177 per cent CaSO₄.

† Plus 0.261 per cent CaSO₄.
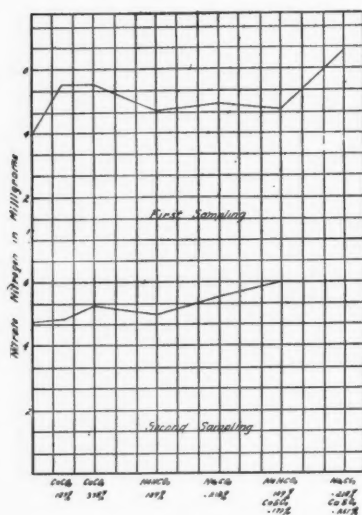


FIG. 12



FIG. 13

FIG. 12. EFFECTS OF CaCO₃, NaHCO₃, Na₂CO₃ AND CaSO₄ ON NITRIFICATION IN ALKALI SOIL—FIRST AND SECOND SAMPLINGS (POT EXPERIMENTS)

FIG. 13. EFFECTS OF CaCO₃, NaHCO₃, Na₂CO₃, AND CaSO₄ ON NITRIFICATION IN ALKALI SOIL—THIRD AND FOURTH SAMPLINGS (POT EXPERIMENTS)

occurred at the second sampling, but the difference was too small to be considered significant. The laboratory tests showed a stimulative effect of 0.518 per cent of $Na_2SO_4$ on nitrification but the effect evidently disappears after the salt has been in the soil for several months and a slight toxic effect is found from this amount of this salt. $MgSO_4$ gave a beneficial effect on nitrification at all samplings except the second, and this is in accord with the results secured in series III, where 0.022 per cent of $MgSO_4$ gave a distinct increase in the process. The effect was not so great here and evidently the beneficial influence of the salt gradually decreased as the time since application increased. After a still longer period it is possible that there would have been no effect whatever or the opposite influence from this salt, just as was noted with the $Na_2SO_4$.

$CaCO_3$ in all cases gave a pronounced increase in nitrification and this result checks with that secured in the laboratory test. The effects of this salt evidently persist for a longer period after it is applied to the soil than is the case with the other salts just mentioned. This salt is so essential in soils for the process of nitrification to occur to the best advantage that its effect in increasing the process is easily understandable.

When all four salts were applied together there was no effect on nitrification. The beneficial effect of the calcium carbonate just noted was not apparent in the presence of the other salts. The slight toxic effect from the $Na_2SO_4$ noted when it was used alone evidently increases in the presence of calcium carbonate and this is offset by the beneficial influence of the $CaCO_3$. Harris (4) found this fact to be true in his tests of the alkali salts on crop growth. It also forms a basis for the result secured in series VIII showing the toxic effect of $CaCO_3$ when applied in larger quantities to the alkali soil.

### Alkali soil tests

On examining the results of the nitrification tests in the soils from the alkali pots it is seen that $CaCO_3$ in both amounts used increased the nitrifying power of the soil. The larger amount gave the larger increase in all cases. The gains were generally quite considerable. Likewise, the $NaHCO_3$ gave quite considerable increases in the nitrifying power of the soils. These results are in agreement with the laboratory tests in series V which showed decided benefit to nitrification from the use of 0.10 per cent $NaHCO_3$. That series showed larger amounts than this to be toxic to the nitrifiers and experiments of others have shown that larger amounts are injurious, hence it is evident that this alkali soil does not contain any considerable amount of $NaHCO_3$. With $Na_2CO_3$, very similar results were secured as with the bicarbonate. Distinct increases in nitrifying power were noted at every sampling. These results check fairly accurately with those secured in series VI which showed a stimulation in nitrification from the application of 0.10 per cent and a depression at 0.30 per cent. It is quite possible that the turning point occurred in that case at about 0.30 per cent and that 0.20 per

cent would have shown an increase. Larger amounts of this salt, like the bicarbonate, depress nitrification, and hence it would seem that this alkali soil is not extremely high in this salt. When calcium sulfate was used with the sodium salts, in every case, with both salts there was an increased stimulation in nitrification. The calcium sulfate alone in the laboratory tests in series VII showed no effect on nitrification in the alkali soil, so the effect here is evidently due to the combinations with the sodium salts. Series IX showed a slight increase in nitrification when $CaSO_4$ was applied with $Na_2CO_3$ in the presence of $CaCO_3$, and that result may serve to verify the present. $NaHCO_3$ in that series did not produce this effect. It is apparent from these results that the nitrification process in this alkali soil was not low as a result of any excess of sodium carbonate or bicarbonate. Calcium carbonate in large amounts likewise did not depress nitrification, so the alkali condition is evidently not due to excess of this salt in the alkali soil. The laboratory tests and the tests in the greenhouse soil several months after treatment were in excellent agreement.

### Crop experiment

As has been mentioned, beans were seeded in both the normal and alkali soils in the greenhouse tests. Four separate plantings were made in the

TABLE 12

*Crop results of pots containing normal soils*

| POT NUM-BER | TREATMENT | GREEN WEIGHT OF CROP | AVERAGE WEIGHT OF POTS |
|---|---|---|---|
| | | grams | grams |
| 1 | None............................................ | 33 | |
| 2 | None............................................ | 39 | 36.0 |
| 3 | NaCl—0.005 per cent............................ | 41 | |
| 4 | NaCl—0.005 per cent............................ | 39 | 40.0 |
| 5 | $Na_2SO_4$—0.518 per cent........................ | 31 | |
| 6 | $Na_2SO_4$—0.518 per cent........................ | 31 | 31.0 |
| 7 | $MgSO_4$—0.023 per cent......................... | 49 | |
| 8 | $MgSO_4$—0.023 per cent......................... | 46 | 47.5 |
| 9 | $CaCO_3$—0.189 per cent......................... | 42 | |
| 10 | $CaCO_3$—0.189 per cent......................... | 38 | 40.0 |
| 11 | All four salts.................................. | 35 | |
| 12 | All four salts.................................. | 34 | 34.5 |

alkali soil but the seed refused to germinate. Barley was then seeded, but grew only in the pot receiving $CaCO_3$, and the per cent of germination was very small. No crop results in the alkali soil were secured, therefore.
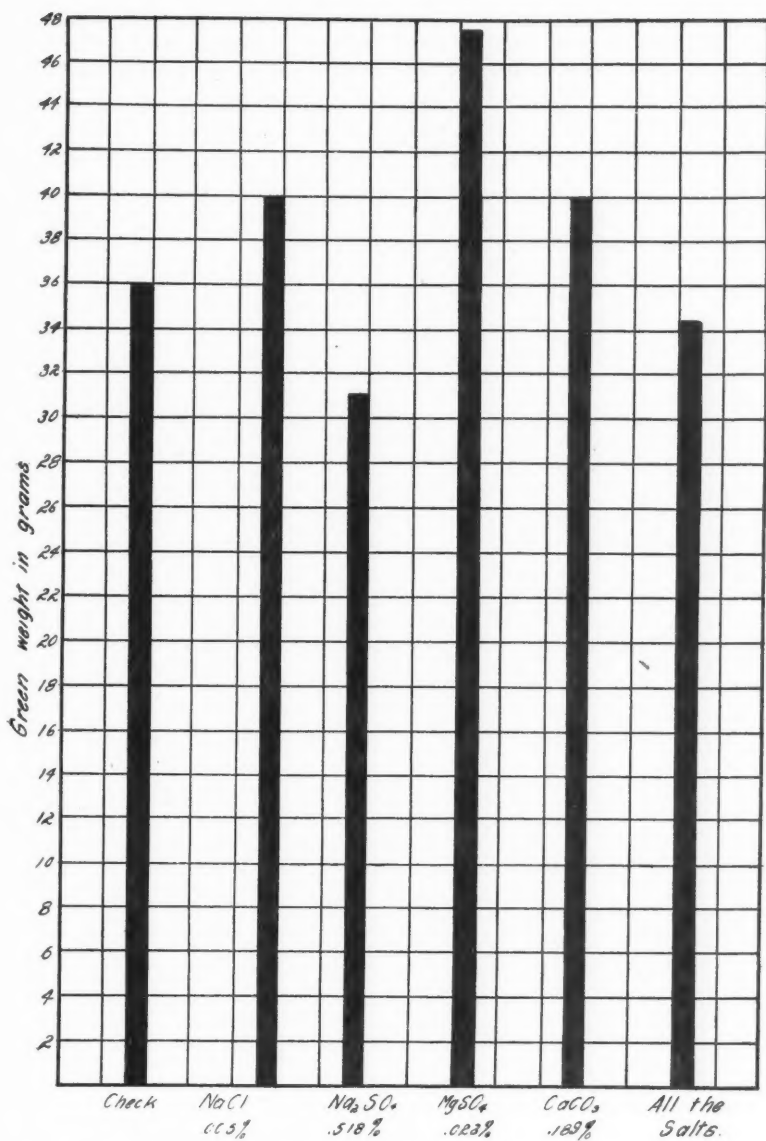
FIG. 14. EFFECTS UPON BEANS GROWN IN NORMAL SOIL WITH THE ADDITION OF VARIOUS
ALKALI SALTS

In the norma soil the bean crop was harvested on February 4, and the green weight secured. The results in table 12 and figure 14 show the crop yields. The NaCl gave an increase in the crop, as did the $MgSO_4$ and $CaCO_3$; the $Na_2SO_4$ depressed the yield slightly and the combination of all four salts gave no effect on the crop. These results check quite accurately with the results of the nitrification tests in the greenhouse soils and, except for the $Na_2SO_4$, with the results in the laboratory. $Na_2SO_4$ in these latter tests increased nitrification. The amounts of NaCl, $MgSO_4$ and $CaCO_3$ used were beneficial, both to crop growth and to nitrification, while the $Na_2SO_4$ was injurious, except in the laboratory test. All the salts together had no effect. Lipman's (8, 9, 10) conclusion that nitrification tests and crop effects agree, in the case of alkali salt studies is thus confirmed. These crop results agree very well with those of Harris (4) already referred to.

## SUMMARY AND CONCLUSIONS

These studies on the effects of alkali salts on nitrification in a normal soil from Wyoming, and on comparative nitrification in normal soil variously treated and in alkali soil, untreated and treated, gave results which, while perhaps not conclusive, are at least indicative of certain relations in the field. These indications may be summarized thus:

1. Nitrification in normal soil is stimulated by small amounts of NaCl, $Na_2SO_4$ and $MgSO_4$, and large amounts of $CaCO_3$. These salts become toxic, however, at certain points, which undoubtedly vary in different soils. With this soil in laboratory tests the toxic point was 0.02 per cent NaCl, 2.00 per cent $Na_2SO_4$ and between 1.5 and 6.00 per cent $CaCO_3$. The toxic point for $MgSO_4$ was not determined.

2. Nitrification in alkali soil was increased by small amounts of $NaHCO_3$, $Na_2CO_3$ and $CaCO_3$. Calcium sulfate had no effect. These salts became toxic in this soil at 0.30 per cent for both the sodium carbonate and bicarbonate and at 6.0 per cent for the $CaCO_3$. The addition of $CaSO_4$ with the sodium carbonate and bicarbonate, in the proper amount to react with them, prevented any toxic effect from the largest amount used.

3. The tests in the greenhouse soils checked very closely with the laboratory studies in the case of the alkali soils. In the normal soils the agreement was likewise good, except in the case of $Na_2SO_4$. That salt became toxic according to these tests at a concentration of 0.5 per cent. This is a very much 'ower toxic point than was noted above but nearer that found by others.

4. The effect on the crop grown in normal soil of the alkali salts, with the exception of the $Na_2SO_4$, were very similar to the effects on nitrification in both laboratory and greenhouse tests. Increases were secured with NaCl, $MgSO_4$ and $CaCO_3$, but $Na_2SO_4$ caused a depression in crop and in nitrification in the greenhouse soils. All the salts together had no effect. In general, it seems that nitrification and crops are very similarly affected by alkali salts.
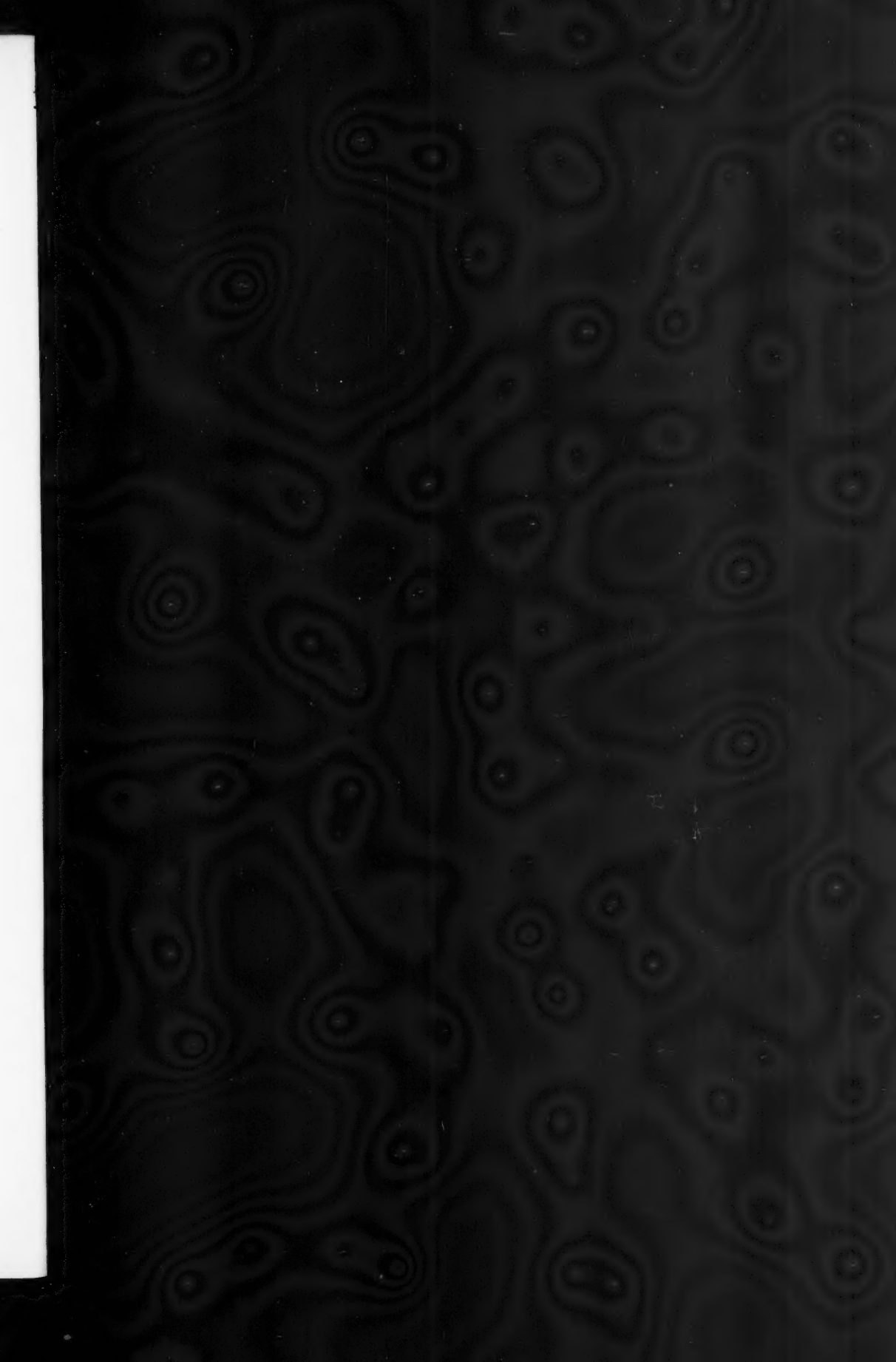
5. Crops refused to grow in the alkali soil, but the injurious factor was evidently not an excess of $NaHCO_3$ or $Na_2CO_3$, as additions of these salts increased nitrification in the soil. The injurious factor was likewise evidently not $CaCO_3$, for that compound stimulated nitrification in the alkali soil.

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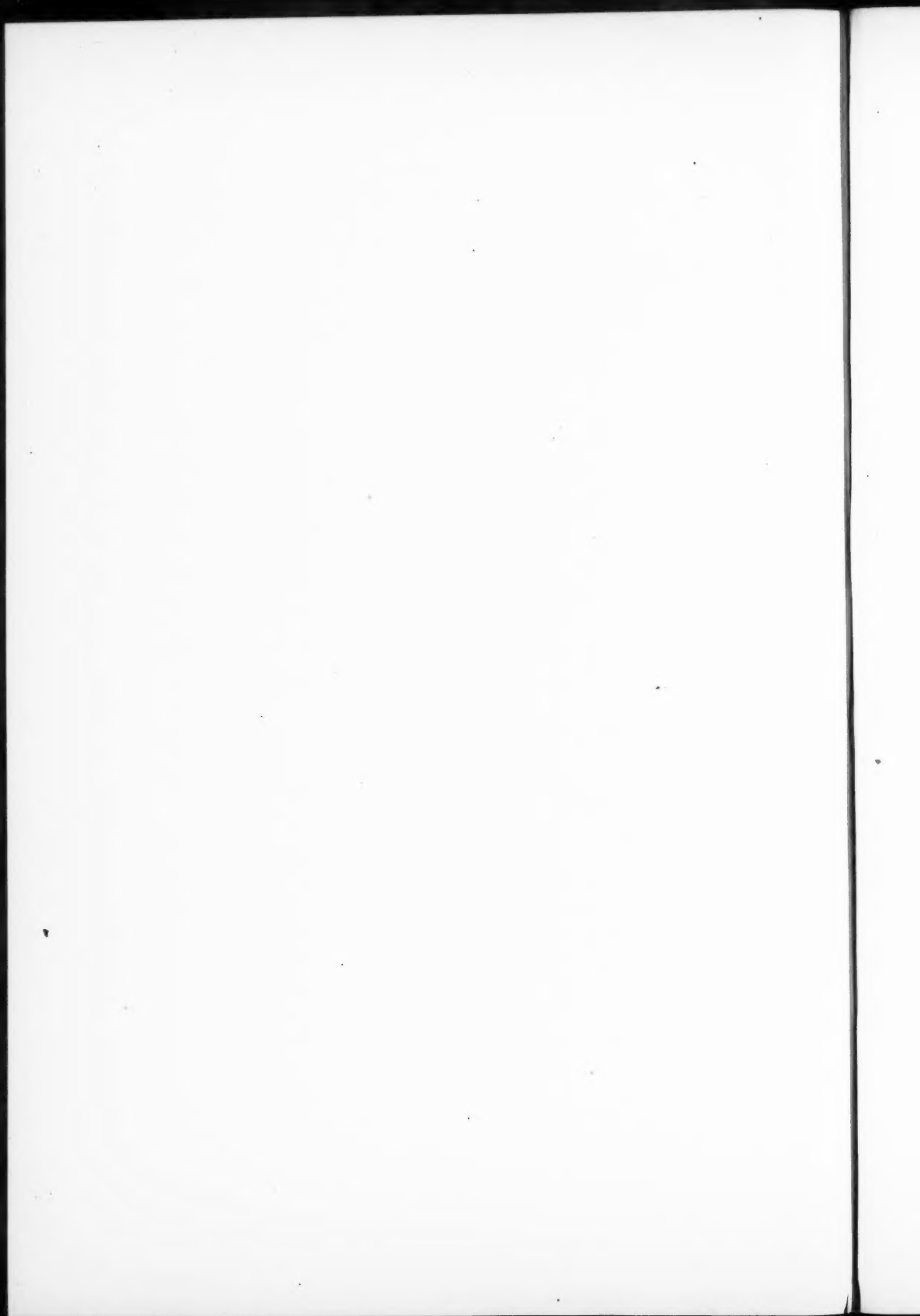
# THE DIVERGENT EFFECTS OF LIME AND MAGNESIA UPON THE CONSERVATION OF SOIL SULFUR

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Until recently scant consideration was accorded the element sulfur in the study of soil fertility. Inaccurate methods of ash analysis, which failed to show the entire amounts assimilated by plants, were probably in a large measure responsible for failure to attribute to sulfur an important rôle in the study of plant needs. It was therefore natural that slight attention should be paid to the form or extent of the element as it occurs in soil. But within the last several years particular attention has been given the subject from the several viewpoints of plant-ash composition, conservation of soil supply, and the amount derived from rainfall. The relationship between soil sulfur and biological activities also has been studied. The Wisconsin, Kentucky, Rothamsted, Ohio, Nebraska, and Iowa stations have contributed to the literature upon the several phases of the subject.

The results submitted in this paper were not obtained from a study which had its inception in a consideration of the sulfur problem. However, the findings as to the behavior of the element during the first two annual periods have been exceedingly striking. It is not intended at this time to offer a complete study or a full array of data obtained, nor of conclusions suggested thereby, but to submit the findings in the way of a preliminary report for the benefit of those who are working upon, or who are particularly interested in, the sulfur problem as related to soil fertility.

Before offering the data obtained, it is essential that a brief description of the experimental equipment and methods followed be given. A mellow sandy loam from the second bench of the Tennessee River at Knoxville was used. One hundred pounds of soil, on the moisture-free basis, were used for each treatment. The lysimeter equipment used in the work is illustrated in plate 1 (figs. 1 and 2). The soil leaching studies now being carried out in the equipment were intended to supplement the work of this station upon the problem of absorption of the several forms of lime and magnesia by soil under field conditions. In the preliminary work, reported upon in part in Tennessee Agricultural Experiment Station Bulletin 107, both 2- and 8-ton applications of lime per acre, or equivalent amounts of the several forms of the earthy alkalies, were made. In the supplementary work here considered, the treatments were based upon chemical equivalences of 8, 32 and 100 tons of CaO per acre. The

excessive applications were made with the idea of affording an opportunity for a study of fundamentals, rather than delimiting the work to bounds which would yield data susceptible of only practical application. The following seven alkali-earth materials were used: burnt lime, burnt magnesia, precipitated calcium carbonate, precipitated magnesium carbonate, 100-mesh limestone, 100-mesh dolomite, and 100-mesh magnesite. Each treatment was thoroughly mixed with moist soil in good, workable condition and placed in a galvanized iron lysimeter containing a sand filter bed, and having a block tin drainage tube. In a second set, placed simultaneously, the foregoing 21 treatments were duplicated as to surface soil, but in this set one foot of clay subsoil was placed between each sand filter and the overlying surface soil. Two additional tanks also were used as separate containers for the relatively inactive natural silicates, wollastonite, and serpentine. Blanks of both depths also were later included.

The successive leachings, derived from natural rainfall only, from July, 1914, to July, 1916, were conveyed to the laboratory, where their respective alkalinities were immediately determined. Aliquots were then preserved in acid solution and the composites for each year were subjected to complete analysis.

In the fifth and sixth columns of table I are given the total alkalinities of the several yearly leachings, expressed as cubic centimeters of half normality. In the seventh and eigth columns are given the amounts of $SO_3$ per acre for the two respective annual periods. A number of tests were made upon the several solutions in order to determine the form of the sulfur present. It appeared that all of the sulfur leached was in the form of sulfates.

A study of table 1 shows certain positive and consistent differences, particularly as to the estoppage effected by the subsoil. During the first year the loss of sulfur was very much heavier from the tanks containing only surface soil than from the tanks which contained subsoil also. As a rule the same holds for the second year; but a marked exception is to be observed in the instances where the oxide and precipitated carbonate of magnesium were applied. The averages of the total amounts of $SO_3$ leached from all the tanks receiving the several carbonates are 472 pounds and 221 pounds per acre, respectively, for the years 1914–1915 and 1915–1916, in the case of the tanks having no subsoil, as compared with 31.1 pounds and 114.8 pounds per acre, respectively, for the identically treated tanks during the same two years where the surface soil was underlaid with one foot of clay subsoil. The material increase in the average of $SO_3$ leached through the subsoil during the second year is due mainly to the fact that during that period large amounts of sulfur began to leach from the tanks containing the treatments of oxide and precipitated carbonate of magnesium, and from these tanks only. Analyses of the leachings established the fact that the downward movement of sulfur and that of magnesium were parallel. That is, where no subsoil was placed, large quantities of both sulfur and magnesium leached out of the surface soil

TABLE 1.

*Alkalinity of leachings and amount of sulfur trioxide leached in two years' tests*

| TANK NO. | TREATMENT | | AMOUNT OF SUBSOIL | TOTAL ALKALINITY OF LEACHINGS— CUBIC CENTI- METERS N/2 | | SO₃ LEACHED— POUNDS PER ACRE PER ANNUM | |
|---|---|---|---|---|---|---|---|
| | Substance applied | Rate- tons per acre | | 1914–15 | 1915–16 | 1914–15 | 1915–16 |
| 1 | CaO | 8 | None | 449 | 604 | 341.0 | 267.0 |
| 22 | CaO | 8 | 1 foot | 102 | 174 | 32.9 | 68.2 |
| 8 | CaO | 32 | None | 1642 | 592 | 19.0 | 116.0 |
| 29 | CaO | 32 | 1 foot | 114 | 98 | 25.0 | 21.6 |
| 15 | CaO | 100 | None | 4301 | 5011 | 67.0 | 15.0 |
| 36 | CaO | 100 | 1 foot | 119 | 105 | 17.4 | 29.5 |
| 2 | MgO | 8 | None | 1024 | 937 | 469.0 | 141.0 |
| 23 | MgO | 8 | 1 foot | 98 | 153 | 40.1 | 161.6 |
| 9 | MgO | 32 | None | 2572 | 4089 | 567.0 | 216.0 |
| 30 | MgO | 32 | 1 foot | 65 | 476 | 18.0 | 488.7 |
| 16 | MgO | 100 | None | 1120 | 2392 | 581.0 | 291.0 |
| 37 | MgO | 100 | 1 foot | 95 | 99 | 24.6 | 228.7 |
| 3 | CaCO₃ | 8 | None | 165 | 434 | 468.0 | 203.0 |
| 24 | CaCO₃ | 8 | 1 foot | 105 | 140 | 34.9 | 58.4 |
| 10 | CaCO₃ | 32 | None | 279 | 442 | 448.0 | 187.0 |
| 31 | CaCO₃ | 32 | 1 foot | 122 | 141 | 29.3 | 30.1 |
| 17 | CaCO₃ | 100 | None | 250 | 399 | 460.0 | 287.0 |
| 38 | CaCO₃ | 100 | 1 foot | 98 | 133 | 27.0 | 124.0 |
| 4 | MgCO₃ | 8 | None | 2207 | 1356 | 528.0 | 170.0 |
| 25 | MgCO₃ | 8 | 1 foot | 98 | 163 | 31.7 | 136.2 |
| 11 | MgCO₃ | 32 | None | 2365 | 3223 | 551.0 | 203.0 |
| 32 | MgCO₃ | 32 | 1 foot | 170 | 451 | 54.9 | 593.6 |
| 18 | MgCO₃ | 100 | None | 2418 | 3833 | 618.0 | 364.0 |
| 39 | MgCO₃ | 100 | 1 foot | 94 | 217 | 38.4 | 409.7 |
| 5 | Ground limestone | 8 | None | 379 | 479 | 540.0 | 214.0 |
| 26 | Ground limestone | 8 | 1 foot | 89 | 128 | 19.5 | 29.1 |
| 12 | Ground limestone | 32 | None | 330 | 459 | 399.0 | 172.0 |
| 33 | Ground limestone | 32 | 1 foot | 111 | 125 | 31.4 | 27.5 |
| 19 | Ground limestone | 100 | None | 392 | 484 | 402.0 | 215.0 |
| 40 | Ground limestone | 100 | 1 foot | 164 | 161 | 40.4 | 87.2 |
| 6 | Ground Dolomite | 8 | None | 230 | 376 | 401.0 | 215.0 |
| 27 | Ground Dolomite | 8 | 1 foot | 101 | 155 | 20.7 | 27.4 |
| 13 | Ground Dolomite | 32 | None | 311 | 548 | 402.0 | 238.0 |
| 34 | Ground Dolomite | 32 | 1 foot | 118 | 122 | 38.8 | 77.7 |
| 20 | Ground Dolomite | 100 | None | 298 | 528 | 417.0 | 325.0 |
| 41 | Ground Dolomite | 100 | 1 foot | 123 | 132 | 26.5 | 18.4 |
| 7 | Ground Magnesite | 8 | None | 489 | 679 | 512.0 | 171.0 |
| 28 | Ground Magnesite | 8 | 1 foot | 118 | 158 | 30.6 | 36.0 |
| 14 | Ground Magnesite | 32 | None | 873 | 859 | 426.0 | 176.0 |
| 35 | Ground Magnesite | 32 | 1 foot | 140 | 178 | 21.1 | 44.6 |
| 21 | Ground Magnesite | 100 | None | 433 | 785 | 509.0 | 181.0 |
| 42 | Ground Magnesite | 100 | 1 foot | 131 | 160 | 22.0 | 21.8 |
| 43 | Wallostonite | 32 | 1 foot | 177 | 170 | 35.3 | 26.2 |
| 44 | Serpentine | 32 | 1 foot | 170 | 174 | 42.1 | 18.6 |

treated with the oxide and carbonate of magnesium during both years.   However, although the subsoil arrested the passage of both magnesium and sulfur during the first year, it permitted the passage of both elements during the second year.   The elimination of the results from the magnesium carbonate tanks materially alters the average of the subsoil tanks for the second annual period. If we average the leachings from the tanks containing treatments of the natural carbonates of both calcium and magnesium and also those containing precipitated carbonate of lime, the alkali earths in all of which are still in large measure retained by the subsoil, we find a loss of 215 pounds per acre for surface soil alone, but a loss of only 48 pounds where the absorption effected by the subsoil is introduced as a factor during the second year of the experiment.   It is thus apparent that the presence of the underlying subsoil either inhibits the formation of magnesium sulfate within the surface soil, or, if not inhibiting its formation, increases the holding capacity of the soil for sulfur, as well as for magnesium; or else the subsoil absorbs not only the basic ion but also the acid radicle.   The first assumption is not tenable, and it is probably beyond doubt that the subsoil has effected an absorption of both Mg and $SO_3$ ions without any interchange of bases, this being confirmed by the analyses of the alkalies in the leachings.

Considering the treatments in the order in which they occur in table 1, the 8-ton applications of burnt lime slightly depress the amounts of sulfur coming through in the leachings, as compared with the other and equivalent treatments; but *the 32-ton and 100-ton treatments practically inhibit the outward movement of sulfur in solution*.   No such retardation in the sulfate leachings was demonstrated by the precipitated carbonate or by the natural carbonate of lime, even in the case of the 100-ton-equivalent applications.   It may be observed that during the second year, when the 32-ton treatment of lime had become in large part carbonated, the increase in the sulfates leached was over six-fold.   It is hoped that we may be able later to state more definitely whether the marked depression is due to chemical or to biological causes, or to a combination of the two agencies.

The effect of oxide of magnesium has been the reverse of that produced by burnt lime.   Either the tendency to form sulfates was engendered or accelerated by magnesia, or else the ability of the soil to retain sulfates has been depressed.   As previously stated, we have observed that the movement of sulfur and that of magnesium are parallel in the leachings so far studied and it is interesting to note that in the case of the 32-ton treatments of both oxide and carbonate of magnesium, the magnesium appeared in the leachings from the subsoil lysimeters in appreciable amounts prior to like appearance in the case of the 100-ton treatments.   The amounts of sulfur leached from these same tanks were in accord with this unanticipated finding of magnesium.

All of the natural carbonates, in the several amounts, appeared to bring about conditions which caused an augmented outgo of $SO_3$, when compared with subsoil tanks which received no carbonate treatment.   The concen-

trations of the leachings during the second year were greater, with reference to their sulfate contents, than during the first year, but the volumes leached during the second year were less than during the initial annual period, so that, as a result, when calculated to the pounds-per-acre basis, the actual amounts of sulfur leached during the second year were smaller than those which passed through during the first year. If the abnormal losses are due to biological activation, such a result would be expected.

The differences between the results produced by the natural and the pre-cipitated carbonates are interesting. The lesser solubilities of the natural carbonates are reflected both in the lack of appreciable increase in the amounts of $SO_3$ leached and in the constancy of the alkalinities of the several leachings. The greater active mass afforded the soil for the satisfying of its absorptive power, in the case of the more soluble oxides and precipitated carbonates, has caused an earlier demonstration of the accelerated movement of alkali-earth sulfates, if, indeed, the natural carbonates are ever to demonstrate such a tendency.

The soil's initial total sulfur trioxide content was 0.1290 per cent, while the subsoil showed a total per cent of 0.1249. The amount of $SO_3$ extracted by a 3-hour agitation with distilled water was 0.0152 per cent for the sur-face soil and 0.0036 per cent for the subsoil. Twenty-gram charges were used in making both determinations.

It can readily be seen that a continued loss of sulfates, in proportions ap-proximating those which have transpired to date, would effect a speedy and absolute depletion of the initial organic sulfur content. Particularly is this true of the oxide and precipitated carbonate of magnesia, while, to date, the excessive burnt-lime treatments are an outstanding exception. In addi-tion, however, to the initial store of organic and inorganic sulfur, there must needs be considered the excessive supplementary aerial supply.

The University farm is located within the boundary of the city of Knox-ville, where a large amount of soft coal is burned. This may be appreciated by the fact that the average of analyses of three years' rainfall by three ana-lysts shows the annual precipitation of sulfur trioxide to be 124 pounds per acre. The analytical data obtained from analyses of the original soil, long exposed to the sulfur of rainfall, do not suggest any characteristic property of this soil to conserve the sulfur obtained from aerial sources.

PLATE 1
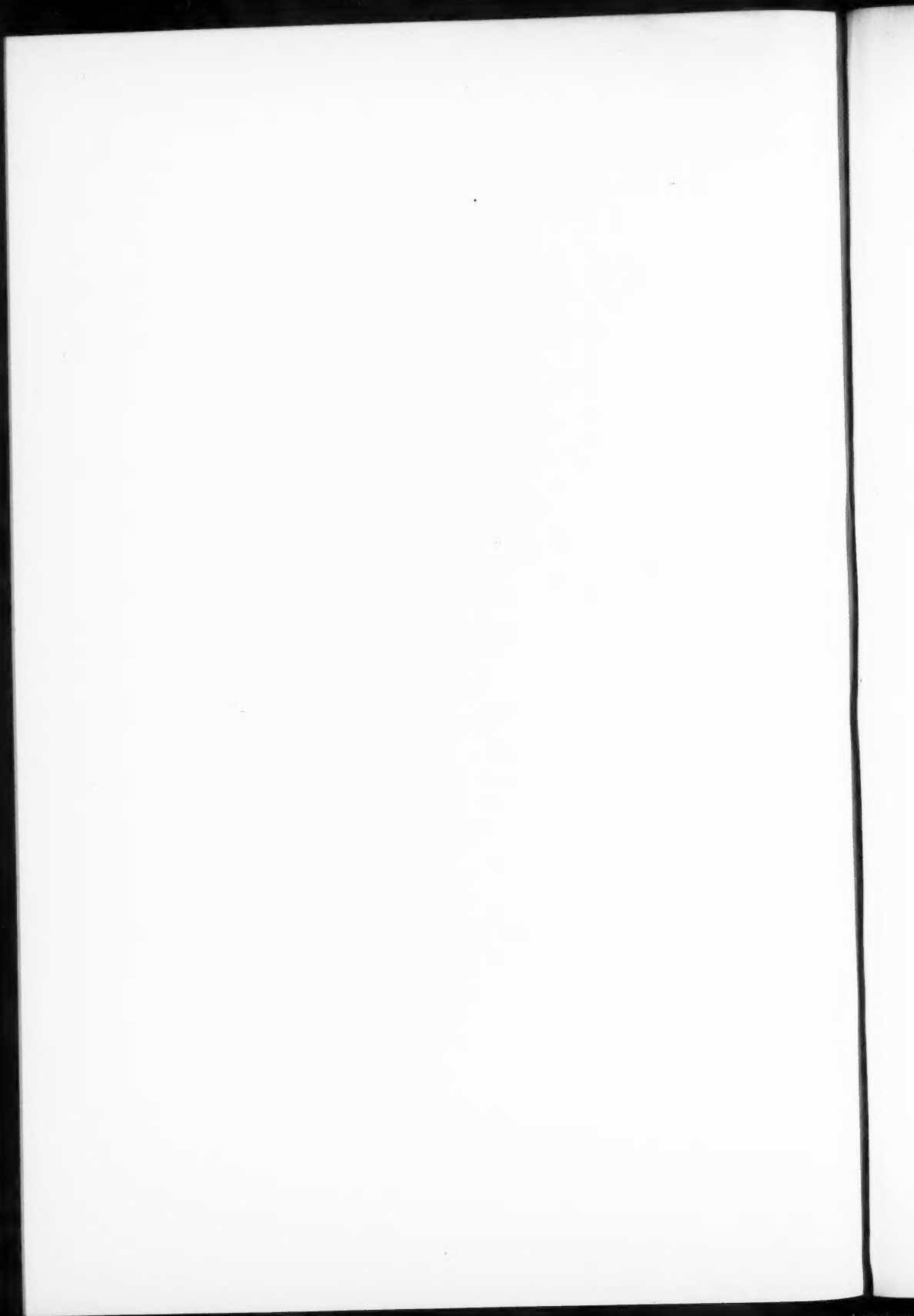
Fig. 1. Outside View of Hillside Lysimeter Equipment
Fig. 2. Inside View of Hillside Lysimeter Equipment

FIG. 1



FIG. 2

# THE RATE OF WATER MOVEMENT IN AERATED SOILS

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Of the many processes operative in soils that are of interest to plant physiologists, those concerned in the movement of water are of primary importance, because they modify the effects of all the other processes upon rooted plants. Furthermore, as has been repeatedly emphasized (5, 14, 15, 16, 17) the ratio between the rate at which water moves from the soil into the plant and the rate at which it moves from the plant into the atmosphere is often of supreme importance in conditioning the existence of a given plant or species of plant in a given habitat. Before any quantitative information of general applicability can be obtained regarding the rates at which plants absorb water from the soil, the preliminary question dealing with the maintenance of intimate contact of absorptive surface and soil water must be answered. Of the two ways in which this contact may be effected, namely, by growth of the roots themselves through the soil as the water is absorbed, and by movement of the soil moisture to the roots, only the second process is susceptible of investigation independently of the other. It thus appears that quantitative knowledge concerning the movement of soil water is of immediate importance to the general physiology of rooted plants. Since *quantitative* knowledge concerning the rates of movement of soil moisture is desired it is important that a definite, quantitative hypothesis concerning water movement be developed, and this is attempted in this paper. The results, combined with experimental data, will, it is hoped, be of service in the elaboration of a more precise, mathematical statement from which the movement of soil moisture may be calculated from measurable soil characters.

In approaching this problem of the movement of water in soils it appears advisable to narrow the field of initial inquiry to non-toxic, non-saline, drained (and aerated) soils because the greater number of higher plants of temperate zones (those that are at present economically and ecologically the most important) are rooted in such soils. The processes by which water movement takes place may be grouped under two heads: mass, or molar movement of water, and molecular movement. The latter, which includes movement by local evaporation and condensation and by diffusion through the soil solution, has, in general, a relatively small effect upon any given plant during its growing season. In the following discussion only molar movement of water will be considered.

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The solution of this problem has been greatly furthered by the work of Briggs (6, 7) and of Buckingham (10). Although these authors obtained no satisfactory quantitative statement of the movement of water, chiefly because they possessed no instrument suitable for measuring rates,[1] their descriptions of the structure of drained, water-containing soils and their very complete analysis of the forces operative in mass movement of water form a valuable basis for such a statement. Obviously, the immediate need is for an instrument that will be suitable for absorbing water from field soils, an instrument whose maximum rate of absorption is greater than the rate of water movement in the soil, whose contact with the soil is intimate and whose absorptive surface remains fixed in position. The high maximum absorption is essential in order that the water may be absorbed as fast as it reaches the instrument so that the rate of movement of soil moisture may be determined. The fixed position of the absorptive surface is essential in order that movement of this surface shall not complicate the analysis of the results of its use, or, as when air is used as an absorbing medium, a dry layer of soil shall not be formed, which diminishes the rate of absorption.

The diffusion of water into a solution from which it is separated by a septum that permits the counter-diffusion of the other components of the solution to only a slight degree has been shown by Pulling and Livingston (19) to be of potential value as the operative principle of such an instrument and was employed in this investigation. The collodion membrane, prepared in the manner described by Bigelow and Gemberling (4) and by Smith (21) was found to be adequate, although a 12-hour immersion in an 80 per cent solution of ethyl alcohol in water, after a certain amount of drying, was found to decrease the permeability and increase the uniformity of the membranes.

In the present studies magnesium sulfate solutions were substituted for those of cane sugar, which were used in the earlier work, because of the high viscosity, great variation in viscosity with temperature changes and chemical unstableness of the latter. Preliminary experimentation, the details of which are not germane to the present discussion, led to the selection of magnesium sulfate in solutions of approximately M.1.5 concentration.[2] As high a concentration as this is not necessary to remove water from the soil, but in order that the instrument might operate for several hours with uniform, water-absorbing power, it appeared necessary that the difference between the specific gravities of the portion of the solution diluted by entering soil water and that of the undiluted portion be great enough to insure rapid operation of convection currents, thus rendering a higher concentration necessary.

The glass thistle tubes used in the Tucson experiments (19), although they

[1] The difficulties of obtaining proper contact between absorbing surface and soil seem to have prevented field tests with the instruments that had previously been described. See Briggs and McCall (8), Livingston (14) and Whitney and Cameron (22).

[2] This solution was obtained by dissolving 1.5 of the gram-molecular weight of hydrated (approximately 7 $H_2O$) magnesium sulfate in 1000 cc. of water at approximately 20°C.

were useful in the preliminary tests, were unsuitable for field use because of their fragility and cumbersomeness.    The form of the instrument that was used
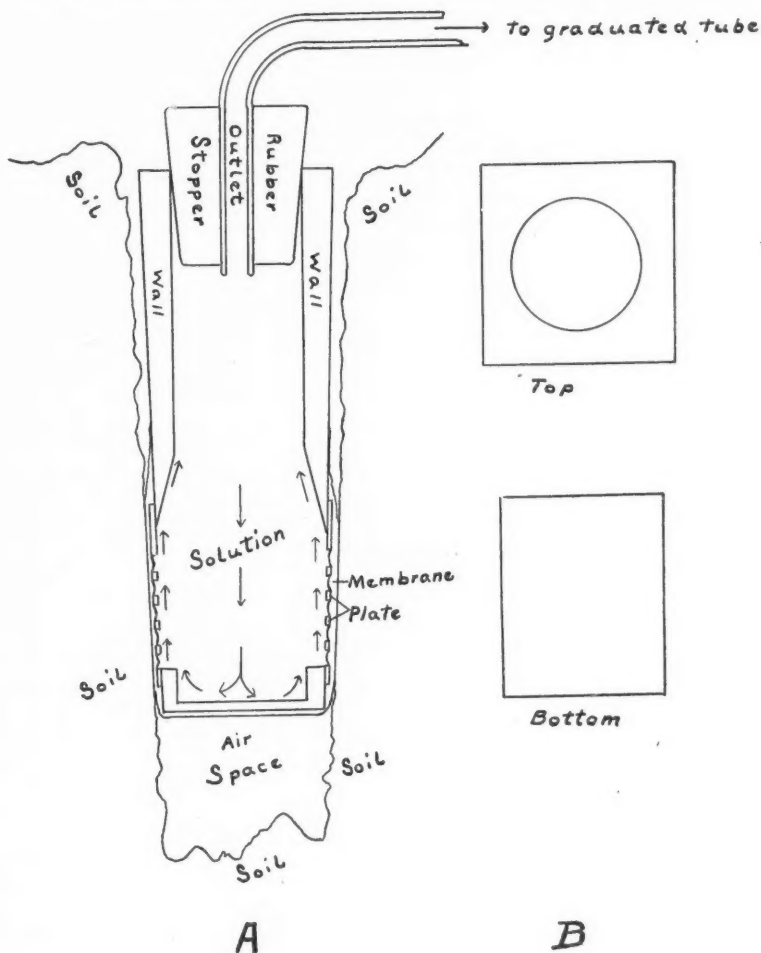


FIG. 1.   THE OSMOMETER

*A*, Sectional view of the osmometer in position in the soil.    The arrows show the approximate general direction of convection currents.    *B*, Top and bottom views of the osmometer.

in the present field tests is shown in figure 1.    Each instrument was made from a bar of brass, square in cross section.    This bar was planed on two opposite faces to form a wedge, $1\frac{1}{4}$ by $1\frac{1}{4}$ inches at the top and $1\frac{1}{4}$ by 1 inch at the

bottom.   A cylindrical core, $\frac{7}{8}$ inch in diameter, was removed longitudinally from the larger end almost to the smaller, and a circular opening, also $\frac{7}{8}$ inch in diameter, was then bored through each of the planed faces, opposite each other and near the lower end, thus communicating with the central cavity. Experimental search for a means to control convection currents (in lieu of stirring) sufficiently to obtain fairly constant rates of intake when the instrument was immersed in water led to the selection of the following as the most convenient.   Thin, brass plates, perforated as extensively as possible with holes $\frac{1}{8}$ inch in diameter, were soldered over the lateral openings.   Although a single membrane was applied over each entire plate, communication with the soil was virtually effected through many small membranes.

To place the osmometers in position in the soil a trench, narrower than the instrument and deeper than its height, was cut with a sharp knife and the soil removed.   The trench was widened until it was only slightly narrower than, and of the same sectional shape as the instrument, which was then carefully lowered into it and gradually, during the course of fifteen or twenty minutes, pushed deeper until further movement was not followed by an increase in rate of water intake, when it was assumed that the greatest possible area of membrane was in contact with the soil.

An objectionable feature of this form of instrument is the flat surface to which the membranes are applied, for the probability that a membrane will adhere perfectly to every part of it is small.   A slight trace of moisture remaining between the membrane and the brass surface forms a drop into which salt gradually diffuses as the instrument is used.   Into this solution water diffuses, enlarging the drop and slowly separating brass and collodion until connection is established with either the interior or the exterior.   If it be with the former, the process proceeds until a continuous passage is formed, underneath the membrane, between the interior and the exterior of the instrument.   Such leaks may be so small as wholly to escape notice while the rate of water intake is great, as in trials of the instrument against water, but may produce large errors when the rates are small, as in many cases of its operation in the soil.

Of the many methods tried for preventing errors caused by these leaks the following was adopted.   Instrument and delivery tube were filled with distilled water and the instrument placed in a small vessel containing water, the upper level of which was above that of the membrane; the graduated delivery tube was elevated until the water meniscus in the tube stood 13 cm. (uniformly maintained but selected from considerations of convenience only) above the water level outside.   The rate at which water passed outward through the membrane (or other accidental exits) as indicated by the fall of the column in the tube, was considered an index of the instrument's permeability.   After considerable experimentation it was decided to discard all membranes that permitted a loss of water at a rate greater than one cubic millimeter per 5-minute interval.   This limit is perhaps so low that many

serviceable membranes were discarded, but as it appeared to be a certain insurance against leaks it was believed best to adopt it. Instruments were tested frequently and whenever one was found that exhibited greater permeability than at a previous test it was considered unsatisfactory and all the data acquired with it during the interim were discarded. Because of these suspected leaks data from less than a third of the original number of tests can be presented.

Turning to a consideration of the movement of water in drained soils it will be of advantage to picture the process descriptively. In such soils
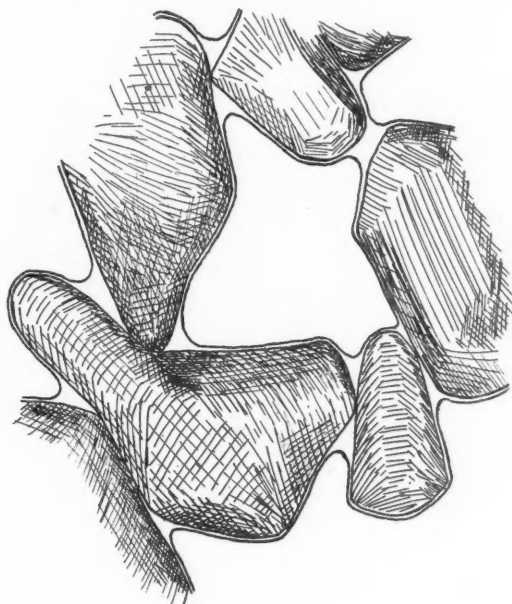


FIG. 2. HYPOTHETICAL SECTION THROUGH A DRAINED SOIL, SHOWING WEDGES AND FILMS

water exists (fig. 2) in the form of thin films covering the soil grains and confluent with masses of water that are of great diversity of form although alike in having an air-water interface concave to the air. Because of their general sectional shape these masses have been termed "wedges" by Buckingham (10) and this designation will be used in the following to distinguish them conveniently from the hygroscopic films that cover the soil grains. Water of hydration, the so-called colloid water and water that has penetrated the minute cracks in the soil grains need not be considered since the water-holding forces that are operative in these cases are so powerful that for present purposes the water may be regarded as virtually a part of the soil grain with which it is

associated. It is necessary only to consider water in the 'forms.'[3] mentioned in the text books as capillary and hygroscopic water, for the third of these forms, gravitational water, is assumed absent since the soil is drained.

As far as plants are concerned the hygroscopic water is of little importance, for, as has been repeatedly shown, they are unable to withdraw it from the soil, as, indeed, a consideration of the elementary principles of equilibrium will demonstrate, and it cannot be reduced in amount by molar water movement. The usual text-book statement is that the "water films" increase and decrease in thickness with varying amounts of soil moisture. The results of investigations on the flow of water in capillary tubes has shown, however, that slipping in the layer of liquid adjoining the wall does not take place, which indicates that relatively strong forces hold it in position. Also Bakker's (1, 2, 3) researches indicate that the thickness of the capillary film is slight (about $1.6 \times 10^{-7}$ cm.)[4] and practically invariable, small variations resulting only in response to large changes in vapor pressure or temperature. Since it is so thin, this film is, throughout its thickness, a fusion of both the gas-liquid interfacial layer of the wedges (the surface tension film) and that water layer of the wedges that immediately adjoins the soil grain. Thus the surface forces resident in the gas-liquid interface of the wedges are transmitted by this hygroscopic film to the soil grains so that the soil mass acquires structure.

In concave surfaces the capillary tension[5] varies inversely as the radius of curvature, becoming least when this is infinite, i.e. when the surface is plane. Since capillary tension is the force retaining water in the wedges, it is evident that for all parts of the soil to be in equilibrium with regard to water movement, the radii of curvature of the concave surfaces (as Briggs long since pointed out) must be equal throughout, regardless of the actual amount of water in any individual wedge or in any number of them. The

[3] As Free (12) has pointed out, references in this connection to forms of water are very objectionable because of the implication that a change of condition or state accompanies change from one form to another, whereas, so far as is known, the difference is solely in the forces (quantitative or qualitative) holding the water in a given position with reference to the soil grains.

[4] This value for the thickness of a capillary film is smaller than that usually given, which ranges from $5–10 \times 10^{-7}$ cm. Quincke (20) gave the distance through which a glass wall attracts water as about $5 \times 10^{-6}$ cm., a much larger value than that of later investigators. The actual thickness is of little importance in this connection since the order of magnitude is practically the same for the different values. For further references and a brief statement of the range of attraction of molecules, see Lewis (13).

[5] *Surface tension* may be defined as the tension per centimeter in the plane surface of a liquid under a given set of temperature and pressure conditions. *Surface energy* is defined as the product of surface tension and surface area. *Capillary tension* is used in this paper to designate the tension, often confused with both the foregoing, brought about by the curvature of a surface that possesses surface tension. Surface tension is thus considered as a property of liquids, varying only with their nature, with temperature and with imposed pressure, while capillary tension varies not only with the surface tension but also with the curvature of the surface.

withdrawal of water from any one wedge will result, in general, in a decrease in the radius of its surface curvature, since almost invariably the space occupied by the water is narrower near the point of contact of the grains than near the air-water interface. This increase in curvature will be accompanied by an increased capillary tension as mentioned above.

A general description of the movement of water in drained soils may now be attempted. As the capillary tension increases the effect will theoretically be two-fold: first, adjoining soil grains that are not in contact (fig. 2) but whose hygroscopic films are a continuation of the surface-tension layer of the wedge and transmit tensions to the grains, will be drawn closer together; and second, water will be moved from adjoining wedges with less curvature (i.e., with greater radius of curvature). In field soils the former process will, in general, be negligible at and below the depths occupied by even shallow-rooted plants so long as forces of greater magnitude than those of capillary tension (such as the expansive force of freezing water) are not active. In the early spring in regions where the soil freezes, in newly-ploughed ground, or on the surface of a dried soil recently wetted, rearrangements of the soil grains would of course be of significance. In general, however, in the deeper portions of the soil the response to the increased tension is movement of water only. Suppose a wedge to be in direct communication with others, the invariable condition in moist field soils of the type considered in this discussion, and suppose water to be removed from the first wedge. Because of the increased capillary tension in the surface of this wedge, water will move into it from the others, through the communications. If these were the only wedges concerned, the first would not obtain sufficient water to compensate for the loss, because movement could proceed only until the curvatures of all surfaces involved became equal, each wedge consequently containing less water than before. If a third set be now considered to be in communication with the second, it is evident that water will move from these wedges to those of the second set, whose radius of curvature becomes thus greater, enabling the first wedge to obtain more water. As additional sets are added to this chain the degree to which the first wedge may, in time, approximate its original water content increases, so that in a field soil, if the amount of water withdrawn is relatively small and the time for recovery is relatively great, the wedges initially depleted will acquire an amount of water practically equal to that originally lost.

If the water is removed, however, by an absorbing body that acts with a continuous and uniform force of absorption, which is, however, not of sufficient intensity to break communication between the wedges, the condition of non-equilibrium should be constant in that portion of the soil immediately adjoining the absorbing body. At any instant of time the air-water interfaces of the wedges touching this body will have the least radius of curvature of any in the soil mass, supposing the soil mass to have been originally in equilibrium. The interfaces of the next wedges will have a greater radius of curvature and the radius will increase from one set of wedges to the next until the unaltered

soil is reached.  As time progresses, the distance through the soil in which
the curvature of the surface has been altered, will increase.  Since the curv-
atures of the surfaces in contact with the absorbing body remain constant
(because the absorbing body acts with a uniform and continuous absorptive
force), the wedge and the absorbing body remaining in practical equilibrium,
it follows that the difference between the curvatures of the air-water interfaces
of any one wedge and the next will continually decrease, since the number of
wedges whose curvatures are unequal will increase with time between the
fixed limits of curvature set by the conditions at the absorbing body and the
unaltered soil.   Since throughout the affected portion of the soil the curvatures
become more and more nearly equal as time progresses, and since the movement
of water is conditioned by the difference between the surface curvatures of
adjoining wedges, it follows that the rate of water movement should become
less and less.   It is also be to expected that the decrease in rate will be most
evident when the number of wedges affected is small.   If, then, the rates
of water movement in the soil were plotted against the corresponding points
in time as abscissas, the resulting curve should exhibit a steep slope during
the first few intervals, the rates decreasing more and more gradually as time
proceeds, until the curve becomes almost parallel to the horizontal axis,
upon which the intervals of time are plotted.   All graphs obtained with the
osmometers exhibit this latter characteristic, those extending over the longest
periods of time showing most plainly the increasing constancy in the rate of
movement.

It is patent, however, from an inspection of the graphs that, although they
are similar in their more general aspects, there are many particulars in which
they differ.   Some are higher than others, some begin with larger rates than
those appearing later in the graph, others with smaller rates; in some the
decline is very rapid, in others it is much more gradual.   The interpretation
of these experimental graphs is divided into four sections.   The first deals
with their general slope, i.e., the rates at which movement of water diminishes
with time.   The second deals with the heights of the graphs, i.e., the actual
amounts of water moved through equal, fixed planes per unit of time.   The
third deals with the observations made during the first few time periods of the
tests.   These initial rates appear to be controlled in their magnitude by con-
ditions other than those considered in sections 1 and 2.   The fourth deals
with the apparent fluctuations in the rate of water movement.

### 1. The Slopes of the Graphs

The movement of water through the soil is opposed by frictional and
capillary resistances.   Since these resistances are chiefly due to the existence
of the soil water in discrete masses it follows that the greater the number of
such masses the greater should be the total resistance, and the slower should
be the rate.   It also follows that if the number of these wedges is initially

great in proportion to the amount of water held, the addition of a unit number will produce less effect than if the number is initially small. As the chief resistance to water movement is probably encountered in moving from one wedge to another, it would appear that the greater share of the time should be consumed in movement between wedges, and not in them. Movement of water must accordingly be pictured as proceeding discontinuously from wedge to wedge, so that a steady state of water movement can never be set up in the soil, although as the rate approaches zero the effect of the lag will be less and less noticeable. So it appears that a consideration of the numbers and volumes of the wedges per unit of gross soil volume is necessary before the preceding general statements can become useful.

Since the wedges are formed about points of contact of soil grains, it is at once obvious that their number will, in general, depend upon the size, shape and number of soil grains in a unit of gross or field volume, since the number of contacts is determined by these variables. In any given case the addition of soil grains in the interstices of a soil mass will result in an increase in the number of wedges, the actual increase depending not only upon the number, size and shape of the added soil grains but also upon the number, size and shape of those already present. Although it appears unprofitable to attempt the formulation of a relation connecting these variables, it seems possible that experimentation may furnish an integration of their various effects as a single, measurable magnitude.

Such experimentation has been made and, although the details must be reserved for another article, the general reasoning and some of the results are of importance in this connection. In a unit volume of any given sample of soil the number of soil grains may be considered to be directly proportional to the weight of the dry soil present in that volume. This would probably be an unjustified statement if very small volumes of a soil consisting of unequal grains were considered. But in a sample having a volume of several cubic centimeters these differences are negligible for ordinary, arable soils, so that these soils may be considered as made up of *average grains*, equal weights of dry soil signifying equal numbers of grains. If two equal volumes of such a soil have the same number of soil particles and the same water content, the number of wedges should be the same, the curvatures of the air-water interfaces should be the same, and water should not move from one sample to the other if they were placed in contact. For soils of heterogeneous composition this statement will be the more nearly true the smaller the amount of water the samples contain; for with small amounts, the water is more closely disposed about the points of contact of the grains.

If samples of some one soil are graded according to their solid content and according to their liquid content, each sample, however, having such a water content that the curvatures of its water surfaces are the same as those of the others (thus rendering their capillary tensions equal), the two series of values (solid content per unit of volume and corresponding liquid content) obtained

may be plotted one against the other to form a graph that may be regarded as exhibiting the variation in the number of wedges per unit of gross soil volume, corresponding to changes in the number of soil grains per unit of volume.   If the curvatures are all the same and the water contents are the same no sample should be able to obtain water from any of the others and each should deliver water at the same rate as the others to a standard absorbing body.

A method has been devised by which such data may be obtained.   By its means samples of a given soil, each of approximately uniform packing may be secured that permit the movement of only about 0.001 gm. of water during 24 hours through an area of about 30 sq. mm. to a standard absorbing body. The liquid and solid contents are then determined for each sample as weights per unit of gross volume.   If the weights of solids per unit of gross volume are plotted for the several samples as abscissas, the corresponding weights of liquid plotted as ordinates, and the points so obtained connected by a line, a curve is produced that is characteristic for the particular soil investigated.   Each soil is thus considered as a three-phase system; solid-liquid-gas, that is defined in any condition of packing and water content when two of the three variables are stated in reference to the entire volume occupied by the three.   These variables should, of course, be stated in terms of volume but for the present the more convenient weights will be used.

By changing the absorbing power of the standard body a family of such curves might be obtained.   These curves will be called the liquid-solid curves, or, more briefly, the l-s curves characteristic of the particular soil from which the data were derived.   Each curve may be considered as exhibiting the change in the number of wedges per unit of gross soil volume that occurs as the number of soil grains is altered, the curvatures of the air-water interfaces remaining the same.   The lowest curve, which is the only one that has been determined, also exhibits the water content for each solid content of the given soil below which the rate of water movement can be considered negligible. Because of its importance this curve should be specially designated, and since it is the lowest of the family it will be termed the $\alpha$ l-s curve, or, briefly, the $\alpha$ curve, and the water content corresponding to any ordinate value thereon will be termed the $\alpha$ water content of the soil for the corresponding solid content per unit of gross volume.

A statement of the rate of decrease in the amount of water moving through a given area in the soil in unit time into an absorbing body that removes the water as fast as it reaches the body (as an osmometer or root hair may be supposed to act) may now be attempted.   On the basis of the preceding reasoning this rate of decrease will vary inversely with time and also inversely with the $\alpha$ water content for the particular solid content of the soil that was encountered in the test considered.   Or

$$dy/dt = k/mt \tag{1}$$

In which $k$ represents a factor of proportionality, $m$, the proper $\alpha$ water con-

tent, and $y$, the decrease in the rate of water movement during the time, $t$, reckoned from the beginning of the test. For any given test $m$ is a constant and since $k$ is also a constant the equation may be integrated directly:

$$y = k/m \cdot ln\, t + C \tag{2}$$

In which $C$ represents the constant of integration, $ln$ is the accepted abbreviation for "natural logarithm of" and the other symbols have their former significance.

The rate of *water movement* at any instant of time may then be expressed by the equation

$$dx/dt = s - (k/m)\; ln\, t + C \tag{3}$$

In which $x$ represents the amount of water that has moved through the given plane from the beginning of the test until the time, $t$; $s$, the amount that moved through the plane during the first interval of time, an amount that *should* move across in each interval if no decrease in rate occurs. The other symbols have their former significance.

To render equation (3) suitable for experimental verification it must be integrated for a finite period of time. Since, for any one test, $s$ is a constant the integration may be readily performed:

$$x = st - (k/m)\, t\, (ln\, t - 1) + Ct + C'$$

In which $C'$ is the new constant of integration and the other symbols have their former significance.

When $t = 0$, $x = 0$ and accordingly $C' = 0$
When $t = 1$, $x = s$ and since $s$ is defined as the rate during the first interval of time

$$x = s + (k/m) + C$$

for during the first interval of time $t = 1$ and $ln\, 1 = 0$. Accordingly
$C = - (k/m)$, and the complete equation becomes
$$x = st - (tk/m)(ln\, t - 1) - tk/m$$

or, rearranging,

$$x = st - (k/m)t \cdot ln\, t \quad \text{[see footnote 6]} \tag{4}$$

For any unit interval of time,

$$x_2 - x_1 = s(t_2 - t_1) - (k/m)\,(t_2 \cdot ln\, t_2 - t_1 \cdot ln\, t_1)$$

[6] It will be at once noted that the effects of temperature, changes in viscosity and surface tension, etc., are not considered in the equation. While these variables undoubtedly influence the rate of water movement, it seems inadvisable to consider them in a preliminary study. The data secured in these tests indicate, moreover, that these variables have slight effects compared with fluctuations in the rates and experimental errors, so that it is necessary to ignore them.

or since $t_2 - t_1 = 1$

$$x_2 - x_1 = s - (k/m)(t_2.ln\,t_2 - t_1.ln\,t_1) \tag{5}$$

or

$$s = x_2 - x_1 + (k/m)(t_2.ln\,t_2 - t_1.ln\,t_1) \tag{6}$$

To test the equation, $k$ must be determined and this can be done only with approximate success from the data at hand because of the lack of knowledge concerning the initial rate, $s$, and because of the fluctuation from one period to another in the amount of water absorbed by the osmometer. The physical meaning of these fluctuations will be discussed later, and for the present purpose a smoothed curve will be considered. This smoothed curve should represent the same total movement of water during the entire course of the test as that found by experiment but it should have no inversions, i.e., no ordinate value should be higher than any preceding ordinate value. The fluctuations are thus temporarily looked upon as accidental or non-essential deviations of experimental observations from the true course of a physical process.

Since $k$ has the same value for all tests, at least for each soil, the one exhibiting smaller fluctuations in the observed rates than do the others, should be selected for its determination. Two values for the rates are needed and these are best selected toward the end of the test when the decrease in rate is small, in order that the smoothing may be done with the least error. Constants obtained in this way are, of course, not accurate but the importance of the subject and the difficulty of making field tests justifies the use of what data may be secured even though, from the standpoint of strict accuracy, they may appear inadequate.

Test No. 3 was selected and the rates were plotted between period 30 and the end of the test, period 54. A straight line was then drawn as nearly as possible along the course it was considered the smoothed curve should pass. At period 35 this line had a height of 5.5 units, and at period 52 a height of 5 units. Since $x$ represents the total amount of water absorbed by the osmometer since the beginning of the test to the time at which $x$ is measured, $x_{t=35} - x_{t=34} = 5.5$ cu. mm. and $x_{t=51} - x_{t=51} = 5$ cu. mm. Data for two simultaneous equations of the form of equation (6) are thereby presented for the determination of $k$:

$$s = 5.5 + (k/m)(t_{35}.ln\,t_{35} - t_{34}.ln\,t_{34})$$
$$s = 5.0 + (k/m)(t_{52}.ln\,t_{52} - t_{51}.ln\,t_{51})$$

Combining these equations and rearranging terms

$$5.5 - 5.0 = (k/m)(t_{52}.ln\,t_{52} - t_{51}.ln\,t_{51} - t_{35}.ln\,t_{35} + t_{34}.ln\,t_{34})$$

or

$$\frac{m(5.5 - 5.0)}{t_{52}.ln\,t_{52} - t_{51}.ln\,t_{51} - t_{35}.ln\,t_{35} + t_{34}.ln\,t_{34}} = k$$

By the method of experimentation already discussed to some extent $m$, the $\alpha$ water content of the soil, was found to be 76 cubic millimeters for each cubic centimeter of this soil when the solid content per unit of gross volume was the same as that found from volume samples of the field soil taken when the osmometer test was made. Substituting this value of $m$ and the proper values for the other symbols

$$\frac{76 \times 0.5}{205.4676 - 200.5218 - 124.4390 + 119.8976} = k = 94$$

In the graphs (fig. 3–11) the continuous lines represent the results of calculating $x_2 - x_1$ for the various time periods and the dotted points represent
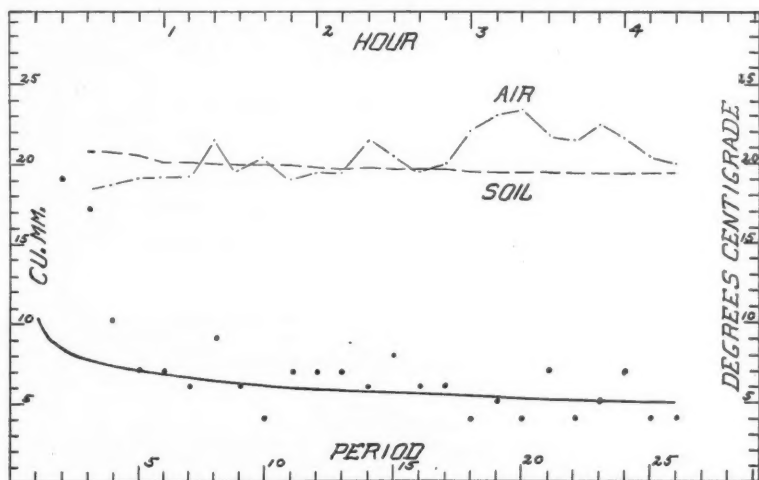


FIG. 3. TEST 1 OF THE OSMOMETER OPERATING AGAINST GARDEN SOIL
Total percentage of moisture on the basis of field volume, 0.193 per cent.

tubes of the osmometers. Remembering that this section deals only with the general *slopes* of the curves, the discussion of their *heights* being reserved for section 2, it will be noted that the graph of the fourth test (fig. 6) is the only one that has a slope notably different from the actual osmometer readings. In this test 0.08 cm. of rain fell during the hour and a half between period 3 and period 12. During the rain the osmometer was covered with canvas which also prevented direct wetting of the soil within two feet of its position. This is of significance when the rates of water intake are observed between periods 13 and 32. About thirty minutes after the cessation of the rain the rates decreased greatly and continued to do so more gradually until period 32 when they became more nearly constant. The speed with which the saturated surface soil attained equilibrium with the dryer soil surrounding
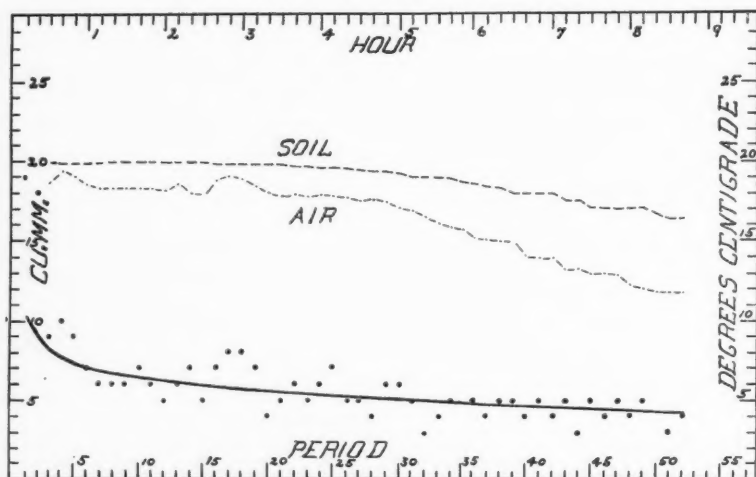
FIG. 4. TEST 2 OF THE OSMOMETER OPERATING AGAINST GARDEN SOIL

Total percentage of moisture on the basis of field volume, 0.200 per cent.
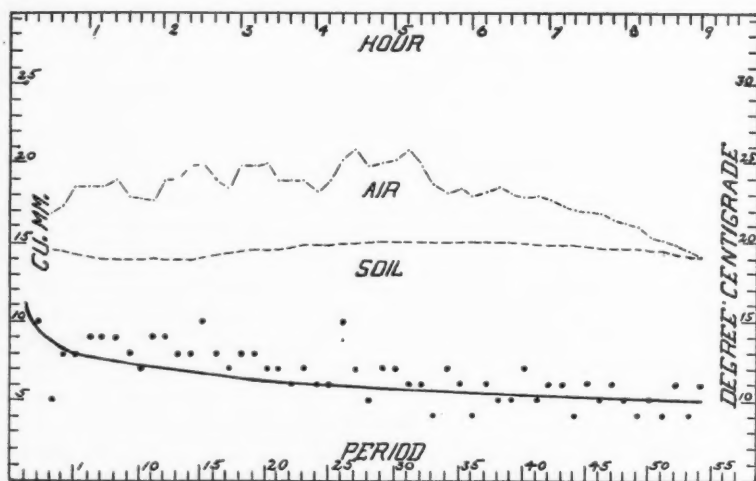


FIG. 5. TEST 3 OF THE OSMOMETER OPERATING AGAINST GARDEN SOIL

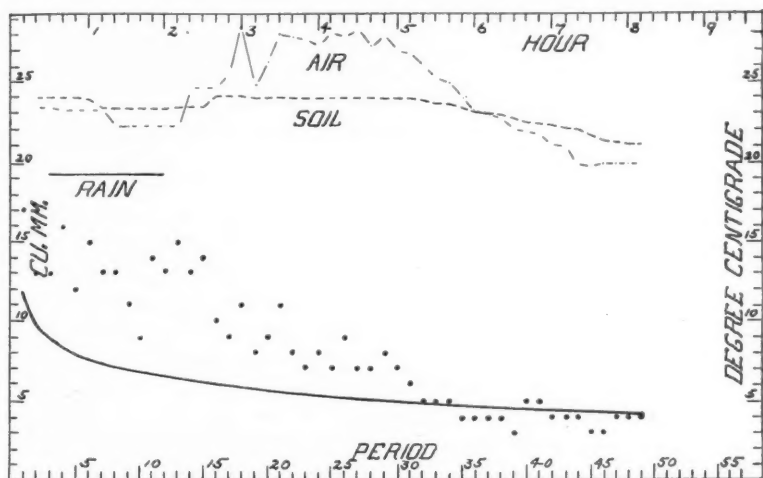Total percentage of moisture on the basis of field volume, 0.213 per cent.

FIG. 6. TEST 4 OF THE OSMOMETER OPERATING AGAINST GARDEN SOIL

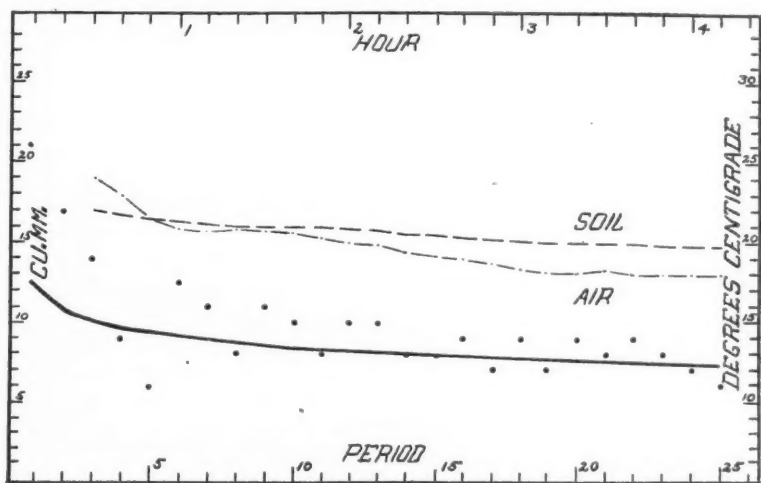Total percentage of moisture on the basis of field volume, 0.211 per cent.



FIG. 7. TEST 5 OF THE OSOMETER OPERATING AGAINST GARDEN SOIL

Total percentage of moisture on the basis of field volume, 0.237 per cent.

the corresponding water intake in cubic millimeters as read on the graduated osmometer (about 2 feet away and about 4 inches below the surface) is indicated by the general decrease in water intake between periods 13 and 32. Unfortunately the rain began so soon after the osmometer was placed in position that conclusions regarding the apparent increase in water intake are not justified, for, as will be explained in section 3, the first few observations on the rates in each test are unreliable.

Although in all cases the general decrease in the rates of water intake as time proceeds are very closely paralleled (with the exception noted above) by the slope of the calculated curve, it is conceivable that the conditions controlling the decrease in rates are wholly different from those considered in formulating the expression by which the calculated curve was obtained. That results calculated with the aid of an equation agree with experimental data is not conclusive evidence that the equation is based upon sound reasoning or justified assumptions. When, however, an equation is successfully applied to a given kind of process under conditions of great diversity, its value as a means of *predicting phenomena* must be recognized. Although the proposed equation has not by any means been thoroughly tested, it has been applied to a considerable range of moisture content for two soils of widely different character. The total volume percentage of soil moisture encountered in these tests ranges for the garden soil between 19.3 per cent and 26.0 per cent, and for the sand between 10.0 per cent and 21.5 per cent, while the value of $m$ ranges between 51 and 77 for the garden soil and 51 and 61 for the sand (table 1). This expression, accordingly, may be considered to have considerable value for calculating the decrease in the rate of soil-water movement unless conditions during these tests were such as are not generally effective in the movement of soil moisture. Of such conditions three groups present themselves as possibly shaping the data: conditions introduced by the instrument, conditions of temperature and conditions of evaporation.

It is at first sight possible that during the operation of the osmometer the solution becomes more and more diluted by the entering water, each increment of dilution decreasing the osmometer's capacity to absorb water. During the preliminary experimentation in search of a method for increasing convection this question was very thoroughly considered. Table 2 presents the data obtained from a test of an osmometer constructed as described and figured in this article, operating against water for 11 hours and 20 minutes. The observations were made at intervals of 5 minutes (the intervals in the tests against soil were 10 minutes long) and is representative of the average magnitude and fluctuation of the readings for all the tests with this type of osmometer. They are presented because the time during which this test was made was greater than for any other. It is evident that there is no decrease in rate at all proportional to that observed in the soil tests even though the average intake during ten minutes was several times the rates for the soil tests. It must then be concluded that dilution of the osmometer
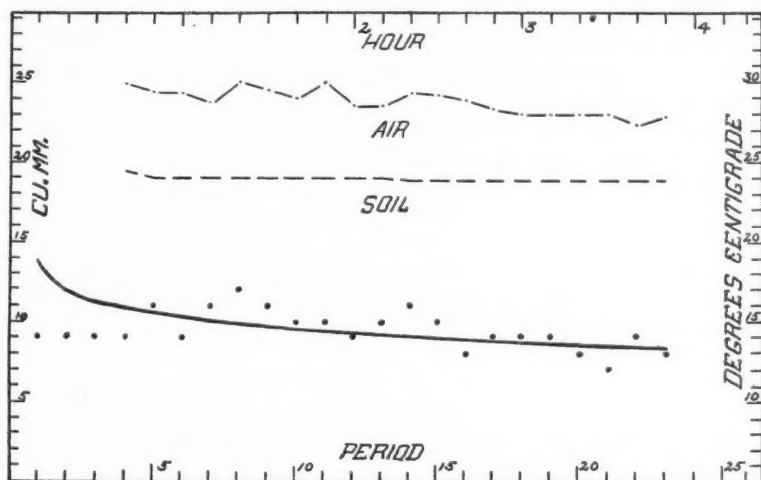
FIG. 8. TEST 6 OF THE OSMOMETER OPERATING AGAINST GARDEN SOIL

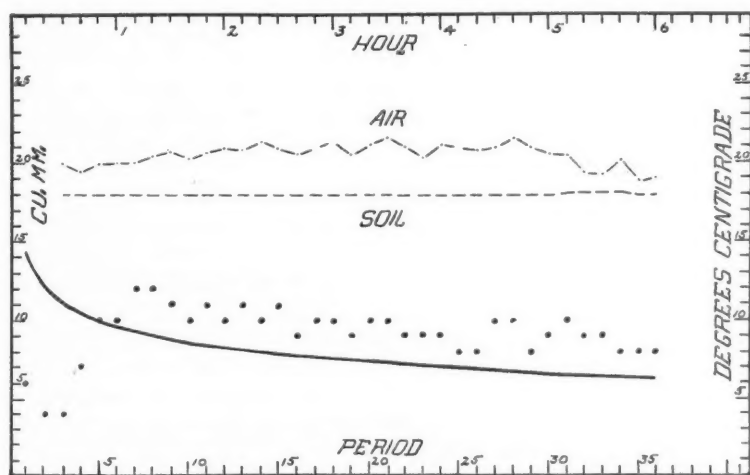Total percentage of moisture on the basis of field volume, 0.260 per cent.



FIG. 9. TEST 7 OF THE OSMOMETER OPERATING AGAINST GARDEN SOIL

Total percentage of moisture on the basis of field volume, 0.257 per cent.

solution is not an explanation of the decrease in rate as observed in the tests with soil.       •

Since temperature is known to affect the equilibrium between solutions and pure solvent when the imposed pressure remains constant, it might seem that temperature changes could be the controlling influence in shaping the graphs (although this effect of temperature probably does not always proportionally affect the speed with which equilibrium is attained for in many cases this rate of solver t entrance may be controlled within wide limits by the membrane, a circumstance not usually considered when the relation between osmotic pressure and root absorption is discussed). There is, however, no evidence that this is true. The temperature curves are not followed by the graphs of osmometer rates, although sudden variations in temperature are often accompanied by corresponding variations in the rates. This latter effect of temperature will be considered in section 4.

The effect of evaporation may be discussed under two heads: the actual depletion of the soil by evaporation from its surface, thus lessening the amount of water available for movement, and the increase in a capillary tension that is transmitted throughout the soil and increases the resistance to water movement. There is little evidence obtainable from these experiments so far as the former is concerned, although there is much general ground for the belief that considerable water is withdrawn from the soil during the course of a day under many conditions. Although a dust mulch very effectively diminishes evaporation from soils, this condition probably was true only in tests 1, 5, 8 and 9, and in the latter two the withdrawal of water by the roots of actively transpiring plants may have offset the effect of the mulch. In tests 1 and 5 the decrease in rate is approximately that calculated, indicating no abeyance of the conditions occasioning the decrease, as would be the case if evaporation were the cause of the diminished rate and a soil mulch were present that prevented evaporation.

Test 4 indicates the extent to which added water influences the rate of movement and may throw light on the question of the effect of withdrawal of water. The day was cloudy and there was almost no wind. The fact that the observed rates near the close of the test are very close to the calculated rates and the speed with which the rates decrease after cessation of the rain, indicate that the water was rather quickly distributed and that the amount precipitated (0.08 cm.) was too small to alter the water content of the soil except locally. It is thus probable that a considerable part of the water that entered the osmometer between the first effect of the rain on the rate and period 30 or 32 was derived from the upper layers of the soil, which later attained approximate equilibrium with the deeper layers. The effect of the rain was thus probably only transitory and without any far-reaching effects. Attention should again be directed to the fact that no data exist for determining the rates *before* the rain and an error in the height of the calculated curve might render the above statements untrue.

The questions concerning a capillary tension transmissible through the soil as such, without concomitant movement of water, its increase by evaporation and the consequent augmented resistance to soil-water movement, may be discussed with the aid of more direct data. Evaporation on sunny days increases during the morning, reaching a maximum intensity early in the afternoon and decreasing toward evening. If the removal of water from the upper layers of the soil by evaporation produces an increase in the capillary tension which is transmitted throughout the soil mass without involving movement of water, it might be expected that movement of soil moisture would
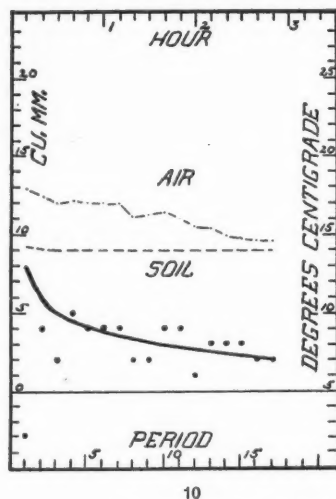



FIG. 10. TEST 8 OF THE OSMOMETER OPERATING AGAINST SAND

Total percentage of moisture on the basis of field volume, 0.100 per cent.
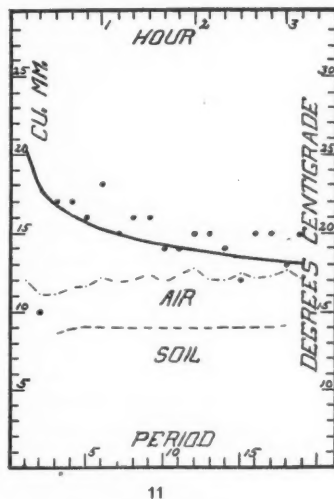
FIG. 11. TEST 9 OF THE OSMOMETER OPERATING AGAINST SAND

Total percentage of moisture on the basis of field volume, 0.215 per cent.

progressively decrease during the day. The rate of this decrease then, should be greatest during the early afternoon, or if it is assumed that the daily evaporation produces a mulch that decreases this noonday maximum, the diminution in rate should be more rapid in the morning. This latter suggestion finds support in the data from all the tests that were started in the morning, and these rates do not show a more rapid decline early in the afternoon as would be expected if the first of the two hypotheses were true. However, the rates in the tests that were begun in the afternoon exhibit the same sort of progressive decrease, and this does not seem susceptible of explanation on the ground of a far-reaching capillary tension. Since the decline in all cases is

very exactly accounted for in a quantitative manner by the general hypotheses of water movement, the capillary tension hypothesis advanced above may be dismissed, at least until more definite information of its effect is obtained.

## 2. THE HEIGHTS OF THE GRAPHS

An inspection of the graphs suggests at once that the amount of water in the soil is the chief condition controlling their heights. An analysis of the Tucson data (19) indicated that with a soil of a given moisture content, the rate of intake, as might perhaps be expected, varied with the area of the absorbing surface. This led to the idea that the initial rate of water movement depended upon the area of the membrane that was in actual contact with the water of the soil. The resistance of the soil to water movement would, according to this view, not affect the amount absorbed during the first instant of time but would subsequently diminish the rate. Part of the water in the soil must be considered to be held so strongly in position that it does not share in capillary movement. As already noted some of this water is held in the hygroscopic films (or "adsorbed" films) on the soil grains. In addition to this, water may be present in wedges whose air-water interfaces are so greatly curved and each wedge may be composed of so little water that a soil containing only this amount and that in the hygroscopic films can deliver water only at so small a rate that it may be considered negligible. Thus, only water that is present in the soil in excess of the sum of the two amounts just mentioned may be considered movable by capillary urge. This water content permitting but neglible water movement is termed the $\alpha$ water content of the soil and, as already mentioned, an experimental means for its approximation has been found.

If this view is correct, the initial rate of water absorption should be proportional to the $\frac{2}{3}$ power of the amount of water in unit field volume of a given soil in excess of the $\alpha$ content (i.e., proportional to the area of one face of a cube whose volume is that of the water contained in unit gross volume of soil in excess of the $\alpha$ water content). In mathematical form this statement becomes:

$$s = r(a - m)^{\frac{2}{3}}$$

In which $r$ is a factor of proportionality, $a$ signifies the amount of water present at the time of the test in a unit of gross volume of the soil and $m$ represents, as before, the $\alpha$ water content of the same soil when it has the same content of solids as when $a$ was determined. It is, of course, necessary that both $a$ and $m$ be determined by drying the soil to the same extent. Substituting this value of $s$ in equations (4) and (5), the complete expressions, as exactly as it is now possible to formulate them, become

$$x = r(a - m)^{\frac{2}{3}} \cdot t - (k/m) \cdot t \cdot ln\ t \tag{7}$$

$$x_2 - x_1 = r(a - m)^{\frac{2}{3}} - (k/m)\ (t_2 \cdot ln\ t_2 - t_1 \cdot ln\ t_1) \tag{8}$$

In order to evaluate $r$, $s$ must be known for some one actual test. It was not possible to secure experimental values for $s$ (section 3) but an approximation may be obtained by adding to the water intake during any interval of time the calculated amount that the rate had decreased since the beginning of the test, i.e., by substituting the proper values in equation (6). When this is done, using the data for time interval 52 of test 3 (the test that was used to evaluate $k$)

$s = 5 + (94/76) (205.4676 - 200.5218) = 11.1$ cubic millimeters, and

$r = s/ (a - m)^{\frac{3}{2}} = 11.1/26.6 = 0.417$

The continuous lines in the figures for garden soil were plotted from equation (8) using this value for $r$ and the value for $k$ obtained in section 1. In general, the agreement is very close, the noteworthy exceptions being tests 4, 5 and 7. In test 4 the high rates previous to period 32 may probably be explained as an effect of the rain. For the others, unless there was an error in the determination of the moisture content of the soil, the expression is not an accurate statement of the rate of water movement under the conditions obtaining during those tests. The actual water content of the soil was, in both cases, lower than that of test 6 (table 1), although the value of $(a - m)$ was higher in test 7 than in any other test with this soil, which may indicate that since the expression is approximately correct for soils both above and below them in water content, the error is in the determination of soil moisture or soil solids or both. Such circumstances render the loss of more than two-thirds of the data, because of leaking osmometers, regrettable.

Turning to the tests with sandy soil, it will be noted that they exhibited a higher rate than was to be expected from the magnitude of the values obtained for $(a - m)$ (table 1). Test 9, for example, had a total water content only slightly higher than $(a - m)$ for test 7, yet the rates were much greater. The most obvious possibility is that $r$ must not be regarded as a universal constant for all soils, but that it varies in magnitude from one to another. The value of $r$ was accordingly redetermined, the data obtained in test 8 being used. The rate at period 17 was taken from the osmometer data and this, with the corresponding values for the other symbols, was substituted in equation (6).

$$s = 2 + (94/61) (48.1644 - 44.3616) = 7.9$$
$$r' = s/ (a - m)^{\frac{3}{2}} = 7.9/11.5 = 0.686$$

When this value of $r'$ is used for test 9, the other test with sand, the value obtained, 20.2, for $r^1 (a - m)^{\frac{3}{2}}$ is found to be in good agreement with the value of $s$, 20.1. This indicates a characteristic difference between the two soils since the value of the constants appears to hold over a considerable range of soil moisture, the entire range for which they have been tested.

The variation in $r$ from one soil to another introduces another obvious

limitation to its use as a constant: it contains no statement of the degree of
soil moisture that will produce the highest rate possible.   It is apparent that
when a certain amount (perhaps characteristic of a given soil) of water is
added to a unit volume of soil by displacing contained air, the wedges become
completely confluent, the hygroscopic films disappear and the soil mass loses
its structure, becoming simply a body of water containing soil grains and gas
bubbles.   The surface forces no longer operate in the movement of water but
are effective only in partially conditioning the form and volume of the gas
bubbles.   The soil has then passed beyond the range of moisture content for
which the proposed equation was formulated, for such a soil is undrained.
How sharply this point will manifest itself may only be conjectured.   If this
point is independent of the percentage of solids in the soil mass, it may be
characteristic only of the kind of soil.   It would appear that a marked change
in specific volume should occur at this point and it may be thus quantitatively
the same as the "critical moisture" content of Cameron and Gallagher (11).
If these points *are* identical the volume percentage of the contained water
should vary with the volume percentage of the solids, as is plainly indicated
by these author's observations on wetted and dried soils.   The apparent agree-
ment between the "critical moisture" content and the "moisture equivalent"
of Briggs and McLane (9) cannot be considered real since the method used
by the latter authors (subjection of the sample to great centrifugal force)
must result in a packing of the soil so that this "constant" cannot be deter-
mined for soils with a low percentage of solids if a constant force is employed.

Since there is undoubtedly a variation from one soil to another in the
degree of soil moisture at which surface forces are no longer effective in the
movement of water, there is great probability that, of two soils having the
same value for $(a - m)^{\frac{3}{2}}$, the one that would have the lowest percentage of
water when puddling occurred would exhibit the higher initial rate, for it
would be nearer complete saturation than the other.   These considerations
emphasize the need of further investigations on the "critical moisture" con-
tent of soils, especially with regard to a simplification of the method and the
relation of this point to that at which puddling occurs.

Another explanation for the relatively smaller rate with the garden soil
than with the sand is based upon the decrease in surface tension caused by
the fatty substances of the manures that were applied to the former.   Whether
this had an effect upon the gas-water surface-tension or only upon the solid-
water surface tension cannot be stated because of the meagerness of data,[7]
although it seems at present that the latter is the more probable.

In table 1 and in figure 12 are presented the values of s calculated from the
observed rates and the value of $k$, together with the corresponding values of
$r(a - m)^{\frac{3}{2}}$.   If a straight line is drawn, passing as nearly as possible through
all the plotted values of s in the tests with garden soil it intersects the hori-

[7] Considerable literature on absorption in soils is summarized by Patten and Wagga-
man (18).

zontal axis at the right of the origin.   This may indicate that water may be
present in the soil above the $\alpha$ water content and yet permit of no measurable
absorption by the osmometer or it may indicate that the curve becomes
changed in slope as it approaches the horizontal axis.   A line drawn through
the two values for $s$ determined from the sand tests, however, cuts the origin
almost exactly and in view of the difficulty of obtaining from the present
data information regarding the actual values for $s$ uncomplicated by tempera-
ture effects and errors of observation, it is idle to attempt a conclusion on
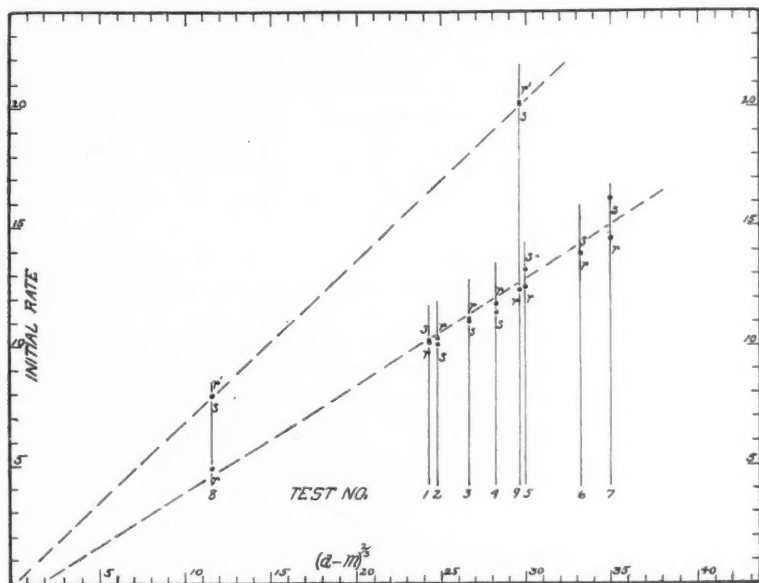this point.



FIG. 12. INITIAL RATES OF THE SOIL TESTS

Points designated $r$ signify the rate was calculated from the expression $r\ (a-m)^{\frac{2}{3}}$ in which
$r = 0.417$, $r'$ signifies the rate was calculated from $r'\ (a-m)^{\frac{2}{3}}$ in which $r' = 0.686$, and $s$
signifies the rate was calculated from equation (6).

### 3. THE HEIGHTS OF THE GRAPHS DURING THE FIRST FEW MINUTES

Apparently the first few observations in each test are not indicative of the
actual movement of water into the osmometer.   To obtain a reading truly
representative of this movement it is necessary that the instrument, when
placed in the soil, shall be at once in full operation and that no change shall
occur in the volume of the contained solution, other than that due to the
entrance of water.   As already noted, complete contact with the soil was
assumed only when movement of the osmometer was not followed by an
apparent increase in the rate.

The temperatures of the solutions used in the tests were lower than those of the soil in every case except those of 6, 8 and 9. The actual amount of these differences cannot be stated, as some change occurred before the osmometer could be placed in position, but since an approximate change in volume of 10 cu. mm. follows a change in temperature of 1.0°C., the probability of large errors in the first few readings is very great. Although no data are available dealing with the temperatures of the solutions used in the tests with sand it is very probable that the soil was much the colder. The soil temperatures were low and the osmometers and solutions were exposed to direct sunshine during the thirty to forty-five minutes required to transport them to the locality at which the tests were made.

Besides the inaccuracies due to causes already mentioned, the observation of the rate during the first time-interval is probably affected by the drying of the soil surface during the time the osmometer was being placed in position, the excess of water on the membrane, due to incomplete removal with absorbent paper, and deficiency of water in the membrane through exposure to the air. These conditions appear to be only temporary and are, perhaps, of slight importance.

#### 4. THE APPARENT FLUCTUATION IN THE RATES OF WATER MOVEMENT

Of the possibilities in this connection, expansion and contraction of the osmometer solution due to changes in temperature are undoubtedly influential. It is impossible to estimate accurately this class of effects because the rate of temperature change in the solution was necessarily slower than the rate of change in the external temperature, so that the volume of the solution must often have been changing in a direction opposite to that in the external temperature. Since there was some change in the temperature of the solutions the fluctuations in the rates must be ascribed at least to some extent to temperature changes.

The changes in volume of the solution were read on a graduated tube made by cutting off the capillary tip of a Mohr pipette, having a capacity of 1 cc. and graduated to hundredths. Since it was necessary to read to thousandths (cubic millimeters) tenths of intervals were estimated. Errors in estimation of a cubic millimeter were accordingly possible, although the probability of frequent errors greater than this is small.

Fluctuation of the observed rates is also possible through the lack of uniformity in the soil. As has been noted, a soil is in equilibrium when the surface curvatures of all the wedges are the same, regardless of the amount of water contained in the wedges. If the soil were perfectly homogeneous, all grains being of the same shape, touching each other at corresponding points and uniformly distributed, the amounts of water forming the wedges would probably be the same. Without question this condition never obtains. Some wedges, because of accidents of shape and arrangement of soil grains contain

more water than others. Uniformity of distribution of either water or soil grains also certainly never occurs. In consequence of this irregular distribution of water it appears inevitable that the same alteration in capillary tension in different portions of a soil will be accompanied by movement of different amounts of water. In such ways fluctuations in the rate of intake by the osmometers may occur.

Changes in the positions of the soil grains consequent upon water withdrawal would decrease the rate of movement from wedge to wedge and this effect should be most apparent in loosely-packed soils. Reference to the graphs will make evident the apparent fact that, in general, the greatest variation is in such soils, but it should also be noted that it is in such soils that the lack of uniformity in soil and water distribution is the greatest, thus producing the effects discussed in the preceding paragraph.

## THE DETERMINATION OF THE PERCENTAGE OF WATER IN THE SOIL ON THE BASIS OF APPARENT, OR GROSS SOIL VOLUME

The usual methods for obtaining the volume percentage of moisture consist of cutting a rather large block of soil, or removing a short column with a tube forced into the soil, or removing a mass of soil with a soil augur. Of the three, the last-mentioned is the best method although it is, like the first, unsatisfactory because small stones and other objects that have no direct effect upon water movement may comprise a part of the soil removed. The first method is also unsatisfactory because the dimensions of the blocks are difficult to determine with accuracy. The second method is of least value since the tube compacts the soil because of friction between the soil mass and the walls of the tube. Compression of the soil in front of the tube will prevent the desired amount of soil from entering and compression within the tube will change the volume of that portion of the soil that is removed, these circumstances preventing any accurate knowledge of the volume occupied by the soil when in its original condition. Packing also occurs when the soil augur is used but to a less extent. The need was accordingly for an instrument with which samples might be removed in practically their original volume. The instrument described below and illustrated in figure 13 was constructed to cut soil blocks quickly and with a high degree of accuracy.

A thin, flat blade of metal was attached to a handle in such a way as to give a rigid surface about 2 inches broad and 4 inches long. This blade was pointed at the tip and sharpened along the sides and tip to a knife edge. A rectangular box, formed from sheet metal with the upper and lower faces open and with the lower (cutting) edge of the remaining four sides bevelled on the outside (so that all compression of the soil in a direction normal to the direction of movement of the cutting edge was avoided), was hinged to the blade in such a way that it would pivot about an axis parallel to the broad surface of the blade. In operating the instrument, this rectangular box was

turned on its axis until it stood at right angles to the broad blade, which was
then forced horizontally into the soil about an inch below the surface. The
box was then swung downward to a horizontal position, thus cutting out a small
block of the soil that lay above the blade. The entire instrument was then
removed, the soil lying outside the box was brushed away, and the soil
projecting above the sides of the box was trimmed with a sharp knife to form
a surface flush with the sides. The weight of the water and that of the soil
contained in the block were then determined in the usual way, by weighing,
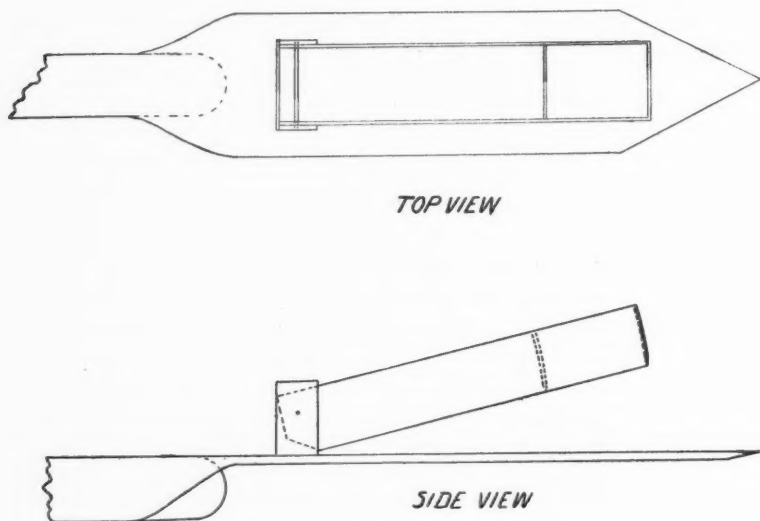drying at 103–105°C., and reweighing.



*TOP VIEW*

*SIDE VIEW*

Fig. 13. Instrument for Obtaining Soil Samples of Known Field Volume

To determine the internal capacity of the box, a block of putty was cut out as
described above, removed, and dropped into a graduated cylinder partly full
of water. The increase in volume of the contents of the cylinder gave the
capacity of the box. Several determinations made in this way indicated
that the volume of the soil blocks was 7.6 cc., the greatest variation observed
being about 1 per cent.

Soil samples obtained in the field were immediately placed in small glass
vials, tightly stoppered with paraffined cork stoppers and weighed indoors
to the nearest centigram within five minutes of the time they were obtained.
They were later dried at a temperature of 103–105°C. in an electric oven in
the same vials with the stoppers removed, cooled in a desiccator over calcium
chloride, the stoppers replaced and again weighed.

## THE SOILS USED IN THESE TESTS

The garden in which most of the tests were conducted had been terraced up to its present height 10 feet above the land below, so that its level was near the summit of the hill of which it had formerly been the steep eastern slope. It had been in constant use as a vegetable garden for over fifty years and had been almost yearly manured with stable manure.   The soil is a very black sandy loam, containing almost no clay, but with considerable amounts of humus.   No test was made within 4 feet of the position of any former test.

The soil termed sand formed a 30-foot hill whose steep northern slope extended down to a river.   This soil is a fine yellow sand and very uniform. A thin (2 to 3-inch) layer of dark, humus-bearing soil overlay the sand and the osmometers were placed with the upper edge of their membranes about an inch below the junction of the two sorts of soil.   Large oak (*Quercus rubra*) elm (*Elmus Americana*) and basswood (*Tilia Americana*) trees grew on this hill in sufficient number to shade the area in which the tests were made.   Near the river *Taraxacum officinale*, several ferns, mosses, *Viola*, *Oxalis*, *Cnicus*, *Ribes Cynosbati* and *Ribes Canadensis* were growing sparsely, and among them test 9 was made.   A portion of the slope was much steeper than the remainder, forming a ridge running back from the water's edge.   Some distance from the river this ridge supported only infrequent clumps of a coarse grass, and here test 8 was made.

### SUMMARY OF FIELD PROCEDURE WITH OSMOMETERS

An osmometer, after being tested for permeability, was filled with M. 1.5 magnesium sulfate solution and carried to the experimental plot (30 to 40 yards in the garden, a few feet when the sand was tested) in water.   A wedge-shaped trench was cut in the soil to a depth of about once and a half the height of the osmometer, i.e., about six or seven inches, and slightly narrower at the top than was the osmometer at its widest part.   The edges of the trench were trimmed with a sharp knife to a plane surface, making it slightly wider at the top than the maximum diameter of the osmometer.   The instrument was then removed from the water, the excess moisture on the surface of the membranes was removed with absorbent paper and it was lowered into the trench until it fitted snugly.   Pressure was carefully regulated so that the natural texture of the soil surface was altered as little as possible.   The remainder of the trench was filled with the earth that had been removed in its formation, some of which was used to cover the entire osmometer except the horizontal graduated tube.   As soon as the instrument was in position an observation was made and further observations were taken regularly during the time the osmometer was in operation.   A thermometer was inserted in the soil within an inch or two or the osmometer's position but in an undisturbed portion and another was hung near the first and close to the level of the ground.

### TABLE 1

*Numerical data for the soil tests*

(Area of membranes 2.863 sq. cm., $r = 0.417$; $r' = 0.686$; $k = 94$; length of period, ten minutes)

| NUMBER OF TEST | SOIL | $a\ (mm)^3$ | $m\ (mm)^3$ | $(a-m)\ (mm)^3$ | $\frac{(a-m)^3}{(mm)^2}$ | $r\frac{(a-m)^3}{(mm)^3}$ | $r'\frac{(a-m)^3}{(mm)^3}$ | $s$ | TIME TEST WAS BEGUN | TIME TEST WAS ENDED |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Garden | 193 | 74 | 119 | 24.20 | 10.1 | | 10.2 | 9.40 a.m. | 2.00 p.m. |
| 2 | Garden | 200 | 77 | 123 | 24.73 | 10.3 | | 10.0 | 12.10 p.m. | 8.50 p.m. |
| 3 | Garden | 213 | 76 | 137 | 26.60 | 11.1 | | 11.1 | 10.00 a.m. | 7.00 p.m. |
| 4 | Garden | 211 | 62 | 149 | 28.10 | 11.7 | | 11.4 | 10.50 a.m. | 7.00 p.m. |
| 5 | Garden | 237 | 74 | 163 | 29.85 | 12.5 | | 13.2 | 3.50 p.m. | 8.00 p.m. |
| 6 | Garden | 260 | 70 | 190 | 33.05 | 13.8 | | 13.8 | 11.15 a.m. | 5.05 p.m. |
| 7 | Garden | 257 | 51 | 206 | 34.90 | 14.6 | | 16.2 | 10.40 a.m. | 4.40 p.m. |
| 8 | Sand | 100 | 61 | 39 | 11.50 | 4.8 | 7.9 | 7.9 | 2.50 p.m. | 6.00 p.m. |
| 9 | Sand | 215 | 51 | 164 | 29.50 | 12.3 | 20.2 | 20.1 | 11.50 a.m. | 3.00 p.m. |

### TABLE 2

*Numerical data of the test of the osmometer operating against water*

(Length of period five minutes)

| PERIOD | CU. MM. ABSORBED | PERIOD | CU. MM. ABSORBED | PERIOD | CU. MM. ABSORBED | PERIOD | CU. MM. ABSORBED | PERIOD | CU. MM. ABSORBED | PERIOD | CU. MM. ABSORBED |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 32 | 24 | 31 | 47 | 32 | 70 | 30 | 93 | 31 | 115 | 28 |
| 2 | 36 | 25 | 31 | 48 | 30 | 71 | 29 | 94 | 28 | 116 | 29 |
| 3 | 35 | 26 | 31 | 49 | 30 | 72 | 30 | 95 | 27 | 117 | 29 |
| 4 | 32 | 27 | 33 | 50 | 30 | 73 | 27 | 96 | 27 | 118 | 28 |
| 5 | 30 | 28 | 31 | 51 | 30 | 74 | 30 | 97 | 30 | 119 | 28 |
| 6 | 32 | 29 | 30 | 52 | 30 | 75 | 29 | 98 | 29 | 120 | 28 |
| 7 | 31 | 30 | 33 | 53 | 30 | 76 | 30 | 99 | 27 | 121 | 27 |
| 8 | 29 | 31 | 31 | 54 | 30 | 77 | 29 | 100 | 31 | 122 | 27 |
| 9 | 32 | 32 | 31 | 55 | 30 | 78 | 28 | 101 | 29 | 123 | 28 |
| 10 | 32 | 33 | 30 | 56 | 30 | 79 | 28 | 102 | * | 124 | 28 |
| 11 | 33 | 34 | * | 57 | 29 | 80 | 30 | 103 | 27 | 125 | 28 |
| 12 | 32 | 35 | 32 | 58 | 31 | 81 | 27 | 104 | 29 | 126 | 28 |
| 13 | 31 | 36 | 27 | 59 | 29 | 82 | 30 | 105 | 29 | 127 | 30 |
| 14 | 31 | 37 | 31 | 60 | 29 | 83 | 29 | 106 | 29 | 128 | 29 |
| 15 | 32 | 38 | 33 | 61 | 31 | 84 | 29 | 107 | 28 | 129 | 27 |
| 16 | 32 | 39 | 31 | 62 | 28 | 85 | 29 | 108 | 29 | 130 | 27 |
| 17 | 33 | 40 | 30 | 63 | 29 | 86 | 30 | 109 | 29 | 131 | 28 |
| 18 | 32 | 41 | 30 | 64 | 32 | 87 | 27 | 110 | 28 | 132 | 27 |
| 19 | 31 | 42 | 30 | 65 | 34 | 88 | 28 | 111 | 28 | 133 | 28 |
| 20 | 30 | 43 | 29 | 66 | 30 | 89 | 30. | 112 | 30 | 134 | * |
| 21 | 34 | 44 | 32 | 67 | * | 90 | 29 | 113 | 28 | 135 | 29 |
| 22 | 31 | 45 | 29 | 68 | 30 | 91 | 29 | 114 | 27 | 136 | 30 |
| 23 | 31 | 46 | 30 | 69 | 30 | 92 | 30 | | | | |

* Column reset to zero.

On sunny days and during rain the osmometer and thermometers were protected by a canvas shade about 6 feet square.

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## EDITORIAL NOTE

Mr. Nicholas Kopeloff, for 18 months assistant editor of SOIL SCIENCE, has accepted service with the United States Department of Agriculture and finds it necessary for this reason to sever his connection with SOIL SCIENCE. The editors wish to express their feeling of indebtedness to Mr. Kopeloff for faithful and efficient service.